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THE INTERFERENCE OF ELECTRONS

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THE INTERFERENCE OF ELECTRONS

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PREFACE TO GERMAN EDITION

In the summer of 1930 it was for the third time found possible to hold a conference in Leipzig, thanks to the official support which was again forthcoming. The subject of this year's conference was the interference of electrons. The publishing firm of S. Hirzel was again kind enough to undertake the publication of the lectures in book form.

It was thought desirable that the lectures should not merely describe experiments concerned solely with the diffraction and interference of electrons, but should consider in detail how far wave mechanics can contribute to the explanation of the electronic conductivity of metals. The first four lectures were accordingly given by Rupp, Wierl, Mark, and Mott, the series being concluded with lectures by Grüneisen, Bloch, and Peierls. Rupp deals not so much with the diffraction of electrons by crystals as with the special phenomena which are observed with slow electrons. He was thus led to give an account of the discontinuity of potential at the surface of the diffracting substance; this gave rise to an interesting discussion on the structure of the surface field, in which von Laue, Bethe, and Joffé took part. Here, as always, the lecturers subsequently incorporated the results of discussion in their papers. Wierl gives an account of his experiments with free molecules, which, apart from their importance in connexion with the measurement of intramolecular distances, make it necessary (just as in the case of X-rays) to consider the behaviour of the atomic scattering factor for electrons. What theory has to say on this last problem is discussed by Mott in the fourth paper; he shows that no contradiction arises and that the properties of the atom form factor are actually reproduced by the theory, for both X-rays and electron beams. Previous to this, however, comes Mark's paper, in which he describes the refinements which, as is well known, have to be made in the simple classical theory of crystal diffraction if the interference of secondary waves is to be taken into account. He considers in

detail what results capable of experimental verification it is possible to deduce from the Darwin-Ewald dispersion theory of X-rays and Bethe's dispersion theory of electron beams.

The first of the three reports on the behaviour of electrons in metals is a paper by Grüneisen, which is chiefly concerned with a comparison of the experimental results on the electrical and thermal conductivities with the results of the modern interference theory. There is no doubt that Sommerfeld's striking advance in this direction, together with the work which has resulted from it, has very notably promoted our understanding of the phenomena exhibited by metals. It is equally certain, however, that there still remains a whole series of problems raised by experiment, towards the solution of which theory has as yet contributed the merest hints or nothing at all. Accordingly, Bloch's paper deals with the mutual action of the electrons, which is usually neglected entirely, although this practice is not justifiable without further examination. Peierls gives an account of the changes in conductivity brought about by a magnetic field, a subject in which our knowledge has been so greatly advanced by the experiments of Kapitza and of Meissner and Scheffers. Here again it is made clear that we are only at the beginnings of a theory, which, however, is extremely valuable even in its present form.

In these papers the reader will find many suggestions for experimental or theoretical work. For this reason I consider their publication in book form amply justified. I wish to express my special thanks to the lecturers for their ready consent, and I have again to thank my assistant, Dr. H. Sack, for his help in organizing the conference and in seeing this book through the press.

P. DEBYE.

LEIPZIG, September, 1930

PREFACE TO ENGLISH EDITION

The subjects dealt with in these papers have lost none of their interest or attraction for investigators since our conference was held. The real cause of superconduction still remains a mystery. On the other hand, Heisenberg has quite recently found a method, based on the Thomas-Fermi distribution, for calculating the atom form factor for the incoherent radiation, a method which is just as simple as that previously known for the coherent part of the radiation. Many other problems will suggest themselves to the readers of this book. That, indeed, is the object of its publication, and I accordingly welcome the extension of its influence by the present English translation.

P. DEBYE.

LEIPZIG, 23rd July, 1931.

CONTENTS

	Page
THE INTERNAL POTENTIAL AND THE ELECTRICAL CONDUCTIVITY OF CRYSTALS (E. Rupp, Berlin: from the Research Institute of the <i>Allgemeine Elektrizitäts-Gesellschaft</i>)	1
ELECTRONIC INTERFERENCE IN FREE MOLECULES (R. Wierl, Ludwigshafen am Rhein) - - - - -	13
THE SCATTERING OF X-RAYS AND OF CATHODE RAYS (H. Mark, Ludwigshafen am Rhein) - - - - -	25
THE ATOM FORM FACTOR (N. F. Mott, Manchester) - - - - -	41
THE EFFECT OF TEMPERATURE ON THE ELECTRI- CAL AND THERMAL RESISTANCE OF METALS IN THEORY AND EXPERIMENT (E. Grüneisen, Mar- burg) - - - - -	45
THE MUTUAL ACTION OF ELECTRONS IN METALS (F. Bloch, Haarlem) - - - - -	63
THE BEHAVIOUR OF METALLIC CONDUCTORS IN STRONG MAGNETIC FIELDS (R. Peierls, Zürich) - - - - -	71
AUTHOR INDEX - - - - -	81
SUBJECT INDEX - - - - -	83

PLATE

DIFFRACTION PHOTOGRAPHS - - - - -	Facing p. 18
-----------------------------------	--------------

The Internal Potential and the Electrical Conductivity of Crystals

E. RUPP, BERLIN

(From the Research Institute of the *Allgemeine Elektrizitäts-Gesellschaft*)

According to the phenomena obtained we distinguish two types of interference between electrons in crystals, interference with "fast" electrons (over 5000 volts) and with "slow" electrons (from 500 volts downwards). For fast electrons the position of the diffraction bands is completely determined by the equations for the interference of X-rays, provided we replace the wave-length in these equations by the velocity of the electrons in accordance with de Broglie's equation. According to de Broglie, any electron moving with velocity V (in "volts") may have assigned to it a wave-length given by

$$\lambda = \sqrt{\frac{150}{V}} \cdot 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation has recently been tested very thoroughly by Ponte* for powdered zinc oxide and is found to agree with experiment to three parts per thousand.

• Experiments on the diffraction of electrons below 500 volts, however, show that here the ordinary interference equations no longer suffice. The first experiments on metals† showed that the wave-length calculated theoretically is greater than that found by experiment, and that the slower the electron, the greater the discrepancy.

The Refractive Index for Electrons

These deviations may, however, still be explained in optical language if we introduce an index of refraction for electron "waves".

* M. Ponte, *Ann. de phys.*, **13**, 395 (1930).

† C. J. Davisson and L. H. Germer, *Phys. Rev.*, **30**, 705 (1927).

We shall explain the effect of the refractive index for a simple case in more detail,* namely for the case where electrons are reflected from a crystal surface in such a way that the angles of incidence and reflection are equal. Then two of the three indices of the reflecting surface of the crystal are equal to zero, i.e. those which lie in the reflecting plane. Let the third index, denoting translation at right angles to the reflecting plane, be j . If we denote the angle of incidence of the beam of electrons on the crystal surface by θ , the angle between the incident beam in the interior of the crystal

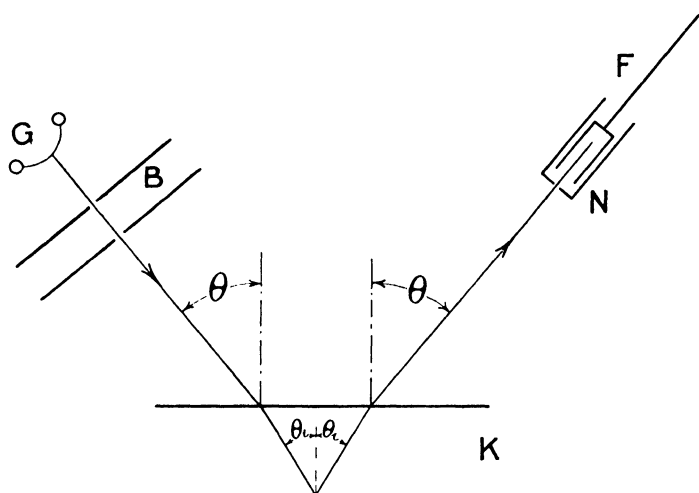


Fig. 1.—Reflection of Electrons of medium Velocity at the Surface of a single Crystal

and the normal to the boundary surface by θ_i , the distance between successive lattice planes of the reflecting surface by d , the velocity of the incident beam by V , the index of refraction by μ , and the wave-length of the electrons outside the crystal by λ , we have the elementary interference equation for the maximum j ,

$$j \frac{\lambda}{\mu} = 2d \cos \theta_i, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

together with the law of refraction

$$\mu \sin \theta_i = \sin \theta. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

These equations, in conjunction with de Broglie's equation, enable us to calculate the refractive index μ from the experimental

* See M. von Laue and E. Rupp, *Ann. d. Physik*, **4**, 1097 (1930).

data if for d we substitute the distances found from X-ray experiments.

To carry out the experiment we let a beam of electrons impinge on the crystal at a constant angle $*$ and vary V , the velocity of the electrons. The number of electrons reflected is measured by means of a collector F (fig. 1), the axis of which makes an angle with the crystal surface equal to the angle of incidence. An opposing field applied to the diaphragm N keeps off slow secondary electrons and electrons which have lost part of their velocity.

As an example of the curves obtained by experiment, the reflection at the plane (111) of a single crystal of nickel for $\theta = 10^\circ$ as found by Davisson and Germer \dagger is illustrated in fig. 2. The

abscissæ represent λ or $1/\lambda$ in Ångstrom units. The wavelength 1 Å corresponds to an electron beam of 150 volts. The positions where theory would lead us to expect diffraction maxima are indicated by arrows. For small wave-lengths, i.e. large

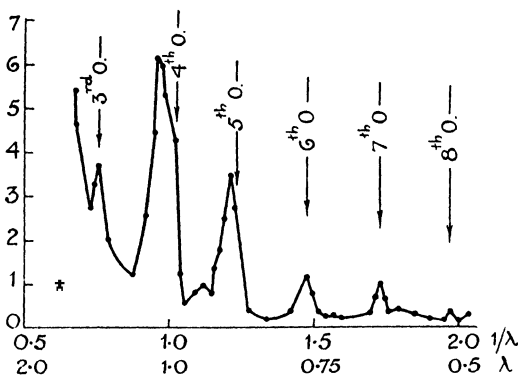


Fig. 2.—Reflection at the (111) Plane of Ni for $\theta = 10^\circ$, according to Davisson and Germer

electron velocities, the arrows coincide with the maxima. For the smaller electron velocities, however, appreciable deviations arise, and these increase rapidly as the electron velocity decreases.

The small maximum of the third order indicated by an arrow is ascribed by Davisson and Germer to anomalous dispersion of the electrons. Here, however, we shall not inquire further into this exceptional case.

The Internal Potential

A physical basis for this empirically-introduced refractive index may be found by deriving it from an internal potential (E_0) in the crystal. According to the wave-mechanics interpretation of the diffraction maxima, μ and E_0 are connected by the equation

$$\mu = \sqrt{\frac{V + E_0}{V}}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

* E. Rupp, *Ann. d. Physik*, **1**, 801 (1929).

† C. J. Davisson and L. H. Germer, *Proc. Nat. Acad.*, **14**, 317, 619 (1928).

If we insert this expression in the interference equation (2) above and replace the wave-length λ by the electron velocity V , we obtain an equation to determine the internal potential, namely

$$E_0 = \frac{150}{4} \frac{j^2}{d^2} - V \cos^2 \theta, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where θ and V are obtained experimentally and d is measured in Ångstrom units.

In the internal potential we have a new experimental quantity associated with the crystal, which gives information about the internal lattice fields, and it is important that numerical values should be collected for various crystals and for various experimental conditions.

E_0 for Metals

The relationships appear to be most simple in the case of metal crystals. Hence a theoretical discussion of the internal potential will have to begin here. We shall therefore proceed to discuss the values for metals.

The accuracy of the measurements of the values of E_0 is unfortunately not all that might be desired. In the calculation of the value of the internal potential from equation (5) all the experimental errors enter into the final result. As the diffraction maxima usually extend over 5–10 volts, V cannot be determined with sufficient accuracy. Small errors in the determination of the maximum of the velocity may often result in large variations in E_0 . Nevertheless, in many of the most recent experiments it has been possible to attain an accuracy to within ± 1 volt.*

If instead of the reflection method mentioned above we use a method analogous to Laue's, the possibilities of error in the determination of E_0 are very much greater, as the diffraction maximum is then determined by three quantities, the azimuth, the altitude, and the electron velocity.

The Effect of Potential Difference on E_0

In what follows we shall compare the effects of potential difference on the values of E_0 for nickel and copper. We have not taken into account the region of anomalous dispersion mentioned by Davisson

* E. Rupp, *Ann. d. Physik*, 5, 453 (1930).

and Germer,* which for the (111) plane of Ni lies between 80 and 100 volts. The results of Davisson and Germer are collected in Table I, while the author's results are given in Table II.

TABLE I

E_0 for Ni (111), according to Davisson and Germer

V	54	65	106	126	160	174	181	190	230	248
E_0	13	16.5	11.5	11	14	13	13	23	10	19
V	248	258	292	310	312	Average				
E_0	28	15	15	16	15	15				

TABLE II

E_0 for Ni (111), according to Rupp

V	41	55	67	78	96	120	122	170	218	220	Average
E_0	17	14	17	20	17	14	16	16	14	20 ± 5	16

All the measurements refer to the same crystal surface, the (111) plane of nickel. The author has also used crystals with a fibrous structure instead of a single crystal.† The value for 220 V found by the author by the photographic method is very inaccurate, as the diffraction rings for nickel were very indistinct.

As the tables show, we can state a mean value for the internal potential of Ni which is independent of the electron velocity within the limits of experimental error. Here the electron velocity was varied between 40 and 350 volts. The author's experiments ‡ on Cu, Ag, Au, Al, Pb, Fe, W§, Mo, and Zr exhibit the same independence of the electron velocity. Here, however, we would expressly emphasize the fact that in the case of these latter metals also there may occur irregular variations in E_0 , which may point to the existence of anomalous dispersion. It is extraordinarily difficult to prove that this anomalous dispersion really exists, and it will be found preferable to ascribe experimental diffraction maxima which give values of E_0 not in agreement with the other values of E_0 to unknown contamination of the surface rather than to anomalous dispersion, and to regard them as unidentifiable.

* C. J. Davisson and L. H. Germer, *Proc. Nat. Acad.*, **14**, 317, 619 (1928).

† E. Rupp, *Ann. d. Physik*, **1**, 801 (1929).

‡ E. Rupp, *Ann. d. Physik*, **5**, 453 (1930).

§ W. Boas and E. Rupp, *Ann. d. Physik*, **7**, 983 (1931).

On the other hand, experiments by Farnsworth * on the (100) plane of copper with electronic reflection, analogous to the Laue method, exhibit a distinct variation of the values of E_0 with the electron velocity. The values are collected in Table III, where the indices given by him are taken as being correct.

TABLE III

E_0 for Cu (100), according to Farnsworth

V	11	27.5	39	45.5	57.2	62.5	70.0	82.5	85	87.5	96
E_0	7.1	5.9	13.5	13.0	15.1	15.1	14.0	14.3	20.1	0	19
V	107.5	110	128	132.5	135.5	176.5	186.5	196.5	206.5		
E_0	26.1	19	25.5	30.2	20.3	21.5	25.7	21.5	27.5		

The results obtained by the author † for the same surface, using the method discussed above, do not exhibit these irregular variations in E_0 , as will be seen from Table IV.

TABLE IV

E_0 for Cu (100), according to Rupp

V	21	55	65	92	125	134	185	208	280	Average
E_0	13	12.5	14	12.8	15	13	12.5	13	(17 ± 4)	13.5

The value in brackets obtained from the photographic method with thin sheets is doubtful.

At the moment it is impossible to say what is the cause of the discrepancy between Farnsworth's experiments and Rupp's. It is of course possible that in Farnsworth's intricate experiments small errors have arisen in the measurement of the angles. Besides, many of the diffraction maxima, e.g. the "extra" maxima with halved order number from 85 V upwards, seem to belong, not to Cu, but to Cu compounds. In the region from 39 V to 85 V a mean value of 14 V holds, and this agrees with the author's value. From 96 V to 206 V a second mean value of 23 V holds, with very considerable variation in the individual results. The maximum at 11 V coincides with the maximum of selective reflection for Cu found by the author, ‡

* *Phys. Rev.*, **34**, 678 (1929).

† E. Rupp, *Ann. d. Physik*, **5**, 453 (1930).

‡ E. Rupp, *Zeitschr. f. Physik*, **58**, 145 (1929).

so that it seems questionable whether this is to be regarded as a diffraction maximum.

The mean values obtained from all experiments hitherto made on metals are collected in Table V.

TABLE V
 E_0 for Metals

Metal E_0	Ni 16	Cu 13.5	Ag 14	Au 14	Al 17	Pb 11	Fe 14	W 12	Mo 13.5	Zr 10.2	K 7.3*	Bi 4†
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The errors in the author's measurements usually amount to ± 1 V. Whether the E_0 -values for electron velocities below about 20 V are valid at all has not yet been proved. We have not taken Rose's value ‡ $E_0 = 0$ for Al into account.

The Effect of Temperature on E_0

Only a few results on the effect of temperature on E_0 are available. The author has found § that in the case of nickel the diffraction maxima do not alter in position between 20° and 350° C., but are merely broadened. It has recently || been shown that for tungsten this behaviour holds good up to 2100° C. Hence it appears that temperature has no effect exceeding ± 2 volts on the value of E_0 .

Comparison of E_0 with the "Work Function" A

According to Sommerfeld's theory of metallic conduction, W_i , the kinetic energy of the conducting electrons, is connected with E_0 , the internal potential, and A , the work of escape ¶ or "work function" measured thermionically or photo-electrically, by the simple equation

$$E_0 = W_i + A. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Here W_i may be calculated from the formula

$$W_i = 26 n^{2/3} a^{-2/3}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

* W. Kluge and E. Rupp, *Phys. Zeitschr.*, **32**, 163 (1931).

† S. Szczeniowski, *C. R. Soc. Pol. phys.*, **3**, 405 (1929).

‡ D. C. Rose, *Phil. Mag.*, **6**, 712 (1928).

§ E. Rupp, *Ann. d. Physik*, **5**, 453 (1930).

|| W. Boas and E. Rupp, *Ann. d. Physik*, **7**, 983 (1931).

¶ *Ger. Austrittsarbeit.*

where n is the number of the conducting or valency electrons of the atom and a the atomic volume.

This equation unites two regions of experimental physics in which entirely differing methods are used. That it agrees qualitatively with experiment is shown by Table VI.

TABLE VI
 E_0 , the Internal Potential, and A , the Work Function

Metal.	E_0	n	W_i	A
Ni	16	$\begin{cases} 2 \\ 3 \end{cases}$	$\begin{matrix} 11.7 \\ 15.3 \end{matrix}$	$\begin{matrix} 4.3 \\ (0.7) \end{matrix}$
Cu	13.5	2	11.2	2.3
Ag	14	2	8.8	5.2
Au	14	2	8.9	5.1
Al	17	3	11.6	5.4
Pb	11	$\begin{cases} 3 \\ 4 \end{cases}$	$\begin{matrix} 7.8 \\ 9.5 \end{matrix}$	$\begin{matrix} 3.2 \\ 1.5 \end{matrix}$
Fe	14	2	11.0	3.0
W	12	2	9.1	2.9
Mo	13.5	$\begin{cases} 2 \\ 3 \end{cases}$	$\begin{matrix} 8.2 \\ 10.8 \end{matrix}$	$\begin{matrix} 5.3 \\ 2.7 \end{matrix}$
Zr	10.2	$\begin{cases} 2 \\ 3 \end{cases}$	$\begin{matrix} 6.3 \\ 8.3 \end{matrix}$	$\begin{matrix} 3.9 \\ 1.9 \end{matrix}$
K	7.3	1	2.1	5.2

In view of the merely approximate validity of equation (7), from which W_i is calculated, and the experimental error in E_0 , equation (6) can only give the right order of magnitude for the work function. It is worth noting, however, that the smaller internal potential of potassium as compared with the values for the other metals, which are all of similar size, is consistent with the greater number of conducting electrons in this metal. Nevertheless, the work function of potassium comes out far too large. Bismuth has been left out of account in the table.

E_0 for Non-metallic Crystals

The simple relationships which hold for metals also appear to hold for semi-conductors which conduct by means of electrons. Here again E_0 is positive, but smaller than for metals.

In the case of insulators,* however, the relationships are more complicated. Here the values of E_0 are negative and approach zero

* M. v. Laue and E. Rupp, *Ann. d. Physik*, **4**, 1097 (1930).

as the temperature of the crystal rises. Probably they do not represent the internal potential of the lattice at all, but a surface charge on the crystal, which will depend in a complicated way on the actual potential, the conductivity of the crystal, and the degree of purity of the surface. Hence all we can do is to regard the values of E_0 as apparent internal potentials. They are, however, a measure of the surface insulation of the crystal, which previously could not be measured. The negative sign is then explained as meaning that the electrons remain sticking in the surface, and the behaviour of E_0 as the temperature of the crystal varies becomes intelligible. As the temperature rises the insulating properties of the crystal decrease; it steadily becomes a better and better conductor. The values of E_0 which have hitherto been obtained for single crystals are collected in Table VII under the headings of electronic conductors and ionic conductors, CuI being regarded as a mixed conductor.

Here again the experimental errors are about ± 1 volt. Within this range it is impossible to prove the existence of any effect of potential difference on the values of E_0 .

TABLE VII
 E_0 for Non-metallic Crystals

Temperature in °C.				20°	80°	200°	270°	370°
<i>Electronic Conductors</i>								
FeS ₂ (pyrites)	+ 6.5				
PbS (galena)	+ 2.6				
Fe ₂ O ₃ (haematite)	+ 3.5				
<i>Ionic Conductors</i>								
CuI (vapour)	+ 2.8				
NaCl (rock salt)	- 4.5	- 3.5	- 3.2	0	0
NaCl (synthetic)	- 3.3				
KCl (synthetic)	- 3.6		- 3.1	0.1	0.0
KBr (synthetic)			- 2.7		
PbI ₂ (vapour)	- 2.0				
PbCl ₂ (vapour)	- 1.4				
TlCl (vapour)	- 0.5				
TlCl (synthetic)		0.0			
LiF (synthetic)		0.0			
CaF ₂ (fluor spar, deep blue)		+ 4.6			
CaF ₂ (fluor spar, almost colourless)	- 4.5	- 3.2	+ 0.1		
ZnS (Zinc blende)	- 5.8				

We shall illustrate the range of error and the way in which the values depend on the potential difference by some experiments

recently carried out on corundum (Al_2O_3) by W. Boas and the author.* The yellowish crystal of corundum was made to reflect from the plane (001) ($a = 11.24 \text{ \AA}$). The angle of incidence was 60° (Table VIII).

TABLE VIII

Al_2O_3 (corundum) for $\theta = 60^\circ$ at 20° C .

V	69	98	106	121	140	158	166	196	208
n	5	7	7.5	8.5	9	11.0	10.5	11.5	12
E_0	-9.8	-9.9	-9.8	-9.0	-9.9	-9.9	-8.9	-9.6	-9.4

In Table VIII V denotes the number of volts associated with the diffraction maxima, n the order, and E_0 the internal potential. The average value of E_0 is -9.5 V . The deviations of the extreme values in E_0 amount to about 10 per cent. Four maxima must be associated with halved order numbers. The reason why numerous orders are amissing is unknown.

In the cubic crystals chiefly used hitherto no relationship between the value of E_0 and the crystal surface used has been found. Whether E_0 varies with the reflecting surface for crystals which are not regular requires further examination.

Characteristics of an Insulator

In the case of an insulator we may raise the question: Can an insulator be distinguished by properties of the elementary lattice?

In distinguishing between conductors and insulators the space group is obviously of no use as a criterion; we need only recall the case of diamond, which though highly insulating, exhibits the same crystal type as silicon, which conducts by electrons. The spacing of the lattice is not decisive either; e.g. spinel (Al_2MgO_4), which conducts by ions, has a lattice constant $a = 8.06 \text{ \AA}$, while magnetic iron ore (Fe_3O_4), which conducts by electrons, has the scarcely greater lattice constant $a = 8.30 \text{ \AA}$.

There exists, however, the possibility of using the internal potential as a criterion. As an example we may mention two crystals of the corundum type:

		a	a	A	E_0	
Al_2O_3	3.51	$85^\circ 45'$	5.15	-9.5 ionic conductor
Fe_2O_3	3.70	$85^\circ 45'$	5.42	+3.5 electronic conductor.

* As regards experimental methods we may mention that the crystal is first thoroughly heated by bombarding it with 10-20-kilovolt electrons and that during the experiment the surface of the crystal is irradiated with ultra-violet light from a tungsten wire to remove stray charges.

The lattice constants differ by only 5 per cent, whereas there is a very marked difference between the internal potentials.

The Relationship between the Apparent Internal Potential and the Electrical Conductivity

The fact that the apparent internal potential is related to the conductivity of the crystal is shown by experiments * on the yellow form of NaCl. Ordinary colourless NaCl conducts by ions, and according to Table VII its internal potential is negative. When exposed to X-rays or electrons NaCl assumes a yellow colour. In this state it exhibits photo-electric conduction by electrons. Thus the electron concentration in NaCl may within wide limits be controlled by the yellow coloration. The question then arises, is the change in the concentration of electrons manifested in the diffraction phenomena? This is actually the case. If we carry out diffraction experiments on strongly coloured NaCl and simultaneously illuminate the crystal with visible light, so that the colour fades, the diffraction maxima are displaced during the fading. Thus, the maximum of the first order moves from 12 volts to 19 during the fading. The position 19 volts corresponds to uncoloured NaCl. From this displacement we may calculate that there is a change in the internal potential from $-2.8 V$ for the coloured crystals to $-3.5 V$ for the uncoloured. Thus as the concentration of electrons in the crystal diminishes so does the value of the internal potential.

* E. Rupp, *Zeitschrift f. Physik*, **61**, 587 (1930).

Electronic Interference in Free Molecules*

R. WIERL, LUDWIGSHAFEN AM RHEIN

1. De Broglie's Equation

The validity of de Broglie's equation

$$\lambda = \frac{h}{mv} = \sqrt{150} \frac{\text{\AA}}{V} \text{ Angstrom units,} \quad . . . \quad (1)$$

which gives the wave-length for an electron with momentum mv accelerated by V volts, has been tested and proved to be accurate to within two or three parts per thousand in the region of the fast cathode rays by various workers (G. P. Thomson, Kikuchi, Ponte). The interesting deviations which are exhibited by the diffraction phenomena for slow electrons and which lead to far-reaching conclusions about the internal lattice potential † are in Bethe's theory ‡ reduced to a rule by the introduction of a refractive index for electrons, given by $n = \sqrt{1 + E/V}$, where E is the internal lattice potential (in metals about 15 volts) and V the potential difference by which the electrons are accelerated. In experiments with electrons having a velocity of several thousand volts the difference between the refractive index and unity is no longer appreciable. Further, the variation of the intensity of the scattered beam for fast electrons with angle has been theoretically established both for elastic scattering (H. Bethe and N. F. Mott§), and for inelastic scattering (H. Bethe), and has also been experimentally determined || from the relationship to the atomic number of the scattering substance.

* A brief announcement of the experiments described here was made in *Naturwissenschaften*, **18**, 205 (1930), and in *Phys. Zeitschr.*, **31**, 366 (1930). A detailed description of the apparatus and of the results obtained has meanwhile appeared in *Ann. d. Physik*, **8**, 521 (1931).

† See the preceding paper by E. Rupp.

‡ H. Bethe, *Ann. d. Physik*, **87**, 555 (1928).

§ H. Bethe, *Ann. d. Physik*, **5**, 325 (1930); N. F. Mott, *Nature*, **123**, 717 (1929), and **124**, 986 (1929); see also N. F. Mott's paper in the present book (p. 41).

|| H. Mark and R. Wierl, *Zeitschr. f. Physik*, **60**, 741 (1930).

Apart from this extensive increase in power of the theoretical treatment, the fast cathode rays possess the practical advantage of easy manipulation, so that now, after but few years of development, certain methods of investigating structure by means of electron waves can be carried out with almost as great precision as has hitherto been possible in the analogous experiments with X-rays. In some respects, notably as regards times of exposure, some of the characteristic features of electron scattering give it a definite superiority.

The interferometric method for measuring the distances between the atoms within a molecule, which was established theoretically by P. Debye* and has been carried out experimentally with X-rays,† can be adapted for the use of electron waves.

2. The Analytical Foundations of Debye's Method

The X-ray analysis of molecular lattices has led in some cases to a fairly definite establishment of the internal structure of individual particles of the lattice, i.e. to the determination of the positions of the atoms in the individual molecules causing the scattering. But this procedure, which consists in exact determinations of intensity by Bragg's method, leads to the desired results only by way of a tiresome elimination and discussion of all the interference phenomena which may arise merely from the symmetrical arrangement of the individual molecules. Even if we get rid of this symmetry by working with the substance in the fused or liquid state, the problem is scarcely simplified at all; for the individual molecules still affect each other's motions, so that phase relationships may occur between the waves scattered by different molecules. The necessary elimination of the resulting interferences, however, can only be discussed on the basis of more exact knowledge of the laws according to which the individual molecules are distributed.‡ The decisive step was taken by Debye in determining the intensity distribution of the X-rays scattered by the substance in the vapour state. The characteristic interference phenomena, for which the "lattice constants" are the distances between the atoms in the individual molecules, are not obliterated even by the completely random nature of the positions of the individual molecules in space. On the other hand, the individual molecules in the vapour are

* P. Debye, *Ann. d. Physik*, **46**, 809 (1915).

† P. Debye, *Phys. Zeitschr.*, **30**, 84, 524 (1929); **31**, 142, 419 (1930); *Ber. d. Sächs. Akademie*, **81**, 29 (1929); L. Bewilogua, *Phys. Zeitschr.*, **32**, 265 (1931); H. Gajewski, *Phys. Zeitschr.*, **32**, 219 (1931).

sufficiently independent of one another for us to ascribe the intensity distribution thus found definitely to "intramolecular" interference unadulterated by "intermolecular" effects.

The general formula for the intensity distribution to be expected is

$$I = K \sum_{i=1}^n \sum_{j=1}^n \psi_i \psi_j \frac{\sin x_{ij}}{x_{ij}}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$$x_{ij} = 4\pi l_{ij} \frac{\sin \theta/2}{\lambda} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here θ denotes the angle through which the beam is deviated, λ its wave-length, l_{ij} the required distance between the atom i and the atom j , and ψ_i the scattering power of the atom i . This quantity (which in the case of X-rays is identical with the atom form factor F) has a distinctive magnitude, and depends on the angle in a distinctive way, for each kind of atom. It also gives the effect which intra-atomic interference has in diminishing the scattered intensity, and is calculated on the basis of a uniform atomic model,

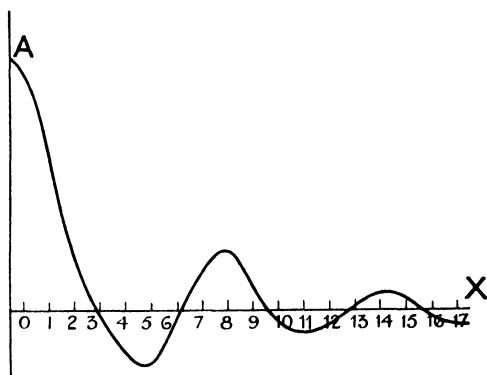


Fig. 1.—Graph of the Interference Function

$$I \frac{\sin x}{x}$$

in which, according to Thomas and Fermi, the electric charge is distributed continuously. In next section this quantity will be re-interpreted and its value calculated for electron waves.

The general procedure in the analysis of molecular structure is then as follows. We assume a definite molecular model (a tetrahedron for the tetrachlorides, a hexagon or pentagon for cyclic compounds), and thence deduce the ratios of the different inter-atomic distances and the number of times each of them occurs in the molecule (periods). If, as in the case of tetrachlorides where the scattering power of the central atom may be neglected (e.g. CCl_4), only one period exists, the distribution of intensity in the diffraction pattern may be expected to follow that of the simple function $\sin x/x$ (fig. 1). The first maximum occurs

at $x = 7.73 = 4\pi l \frac{\sin \theta/2}{\lambda}$. Thus the experimental value of the

angle θ for which the first maximum occurs, together with the wavelength, gives l , the required distance between the atoms (the edge of the tetrahedron). The second maximum comes at $x = 14.0$, so that the ratio of the distances along the x -axis is 5 : 9 and not 1 : 2, as it would be if Bragg's relationship were true. Thus in addition to the position of the minima, which may also be obtained experimentally, several independent quantities are determined in this way.

In general, however, the intensity curve cannot be expected to be as simple as this. Thus for tetrahedral molecules in which the scattering power of the central atom (c) is comparable with that of the corner atoms (e), the general intensity formula is

$$I = K \left(4\psi_e^2 + 12\psi_e^2 \frac{\sin x}{x} + 8\psi_e\psi_c \frac{\sin \sqrt{3/8}x}{\sqrt{3/8}x} + \psi_c^2 \right). \quad (4)$$

The abscissæ corresponding to the maxima are again obtained by graphical superposition of the various functions of type $\sin x/x$, which differ in amplitude and period.

In conclusion, we reproduce the theoretical distribution of intensity for the plane pentagon (as required by the molecular model for cyclopentane) in fig. 2. The heavy curve obtained by superposition according to the formula

$$I = 5K\psi_c^2 \left(1 + 2 \frac{\sin x}{x} + 2 \frac{\sin (\sqrt{5} + 1)x/2}{(\sqrt{5} + 1)x/2} \right), \quad (5)$$

after a strong minimum, exhibits a feeble first maximum and a strong second maximum, followed after a greater interval by a third maximum.

3. The Atom Form Factor

Now although the photographs of electron diffraction, e.g. with cyclopentane, exhibit fairly close agreement with the theoretical diagram as regards the relative positions of the individual maxima, the relative intensities of the various rings are essentially different from those given by the curve obtained by superposition. In general the intensity decreases extraordinarily rapidly as the angle increases. Even the classical theory of the scattering of electrons has something to say about this; according to Rutherford's scattering formula, in fact, it requires that the intensity should decrease in proportion

to $\frac{1}{\sin^4 \theta/2}$, where θ is the angle of deviation of the beam. The results of scattering experiments with atoms of differing atomic number exhibit deviations which are accounted for approximately with the help of a corrected scattering formula $I \sim \frac{Z^2}{(\sin^2 \theta/2 + a^2)^2}$, where the deviation (due to the electronic shell) from the scattering

arising from the atomic nucleus regarded as a point is taken account of by the screening constant a . Hitherto, however, it has been found very difficult in practice to discriminate between particles which are singly scattered and those which are scattered repeatedly. But this whole question has been settled in a very simple way by means of electron diffraction.* For when fast cathode rays are scattered by extremely thin sheets of metal it is only the electrons which are scattered singly and elastically that

are capable of diffraction leading to interference phenomena. Thus measurements of the intensity of the Debye-Scherrer rings certainly include only those singly-scattered particles which interest us here. These experiments were carried out for aluminium, silver, and gold foil by means of a combined electrical and photographic method; they give increasing deviations from the simple nuclear scattering formula $I = Z^2/\sin^4 \theta/2$ as the atomic number of the atoms causing the scattering increases. Bethe's theory also has something to say on this matter. A natural modification of the theory of X-ray scattering (in the case of electrons the potential takes the place of the charge) gives the relationship $I \sim k \frac{(Z - F)^2}{\sin^4 \theta/2}$ for the atom form factor. Thus a term taking

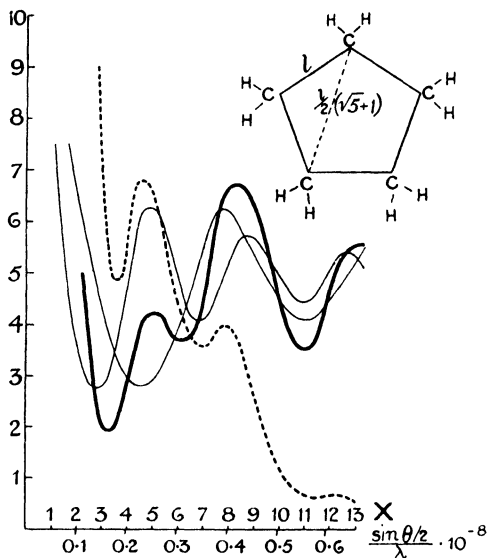


Fig. 2.—Theoretical Distribution of the scattered Intensities for the Cyclopentane Molecule

* H. Mark and R. Wierl, *Zeitschr. f. Physik*, **60**, 741 (1930)

account of the scattering by the electronic shell of the atom has to be added to the formula for the purely nuclear scattering. The quantity F is well known in the theory of X-ray scattering, and, as we have mentioned above, it is very simply calculated from the Thomas-Fermi distribution.* The extent to which the scattering formula has been confirmed experimentally is shown by the graph taken from our paper (fig. 3), in which all the curves coincide at the point 220. The qualitative result is exhibited in fig. 4 (see plate); $a(\text{Al})$ and $b(\text{Ag})$ show the same blackening in the 111-circle. The

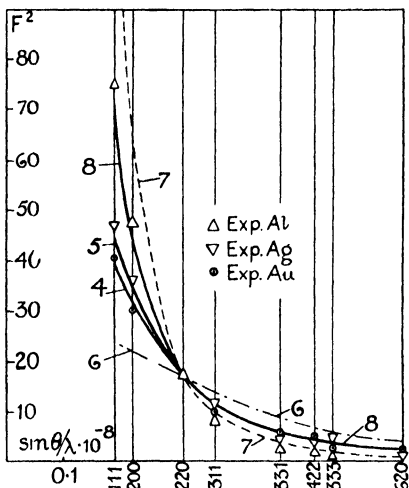


Fig. 3.— F -values for Electrons in the Elements Al, Ag, and Au: curve 7 gives the nuclear scattering alone (Rutherford)

decrease in the coherently scattered intensity is much more rapid in Al (a) than in Ag (b).

The scattering power is accordingly given by

$$\psi_i^2 = K \frac{(Z_i - F_i)^2}{\sin^4 \theta/2}. \quad (6)$$

If there are different kinds of atoms present, each elementary curve must be multiplied by ψ_i before superposition†; in the case of cyclopentane (fig. 2) the dotted curve gives the final graph of the theoretical intensities. As compared with the uncorrected curve, it exhibits displacements of the x -values of the maxima

towards smaller angle values, which, though trifling in amount, are important in connexion with the calculation of the distances between the atoms. In order to make the correction the value of l for each elementary curve must be known; an approximation for it is obtained by means of the uncorrected curve.

The difference in the elementary scattering process for X-rays and for electrons is also manifested in the differing applicability of the two methods to various problems. X-rays are scattered only by the electrons of the atom, the atomic nucleus, owing to its great mass,

* Cf. W. L. Bragg and J. West, *Zeitschr. f. Kristallographie*, **69**, 118 (1928).

† This is most simply done by multiplying the elementary curves, in which $\psi_i \psi_j$ is simply put proportional to $Z_i Z_j$, by the factor $\frac{K}{\sin^4 \theta/2} \left(1 - \frac{F_i}{Z_i}\right) \left(1 - \frac{F_j}{Z_j}\right)$.

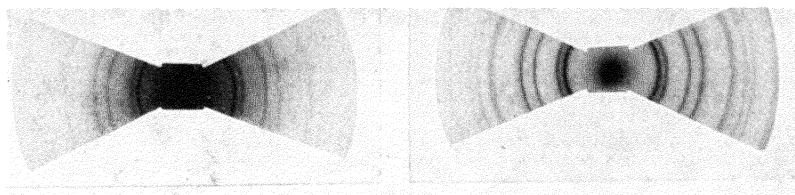


Fig. 4a

Fig. 4b

Electron Diffraction Photographs for (a) Al and (b) Ag foil

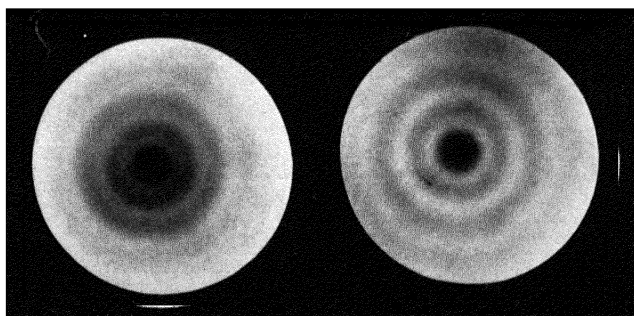


Fig. 6a

Fig. 6b

Diffraction of (a) 54-kilovolt electrons and (b) 40-kilovolt electrons by CCl₄

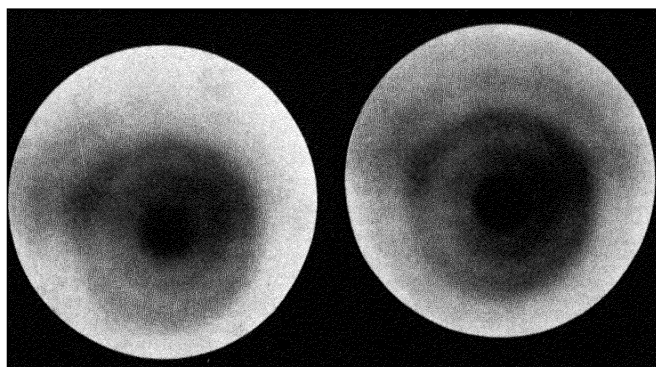


Fig. 7a

Fig. 7b

Diffraction Photographs of (a) 1-1-dichloro-ethane and (b) 1-2-dichloro-ethane

taking no part in the process. In the case of electrons, on the contrary, the nuclear scattering is preponderant, and the effect of the surrounding cloud of electrons only makes itself noticeable in the deviation from Rutherford's formula when the angles are very small. This fact, which may be interpreted as an effect due to the size of the atom, has the result e.g. in the case of benzene (with its small carbon atoms) that phenomena of molecular interference are readily obtained with electrons, whereas the photographs of X-ray scattering in this case merely give a continuous decrease without noticeable maxima. On the other hand, in the case of the more refined questions of atomic linkages, where small differences in the distribution of the electrons of an atom are important, X-rays are a better means of investigation than electrons, as the latter actually give information only about the positions of the atomic nuclei. We may remark, however, that even in the case of the diffraction of electrons by molecules with single and double carbon bonds there arises a small difference in the theoretical curve of scattering, and that this is confirmed by experiment.

4. Electron Diffraction in a Beam of Vapour: (a) Determination of Atomic Radii; (b) Cyclic Molecules; (c) The Problem of Free Mobility

We now proceed to consider experimental methods and the results we have hitherto obtained from our electron diffraction experiments.

Hard cathode rays, generated by an electric discharge through hydrogen in a quartz tube, are stopped down to a fine beam by means of a long narrow tube. Immediately beyond the far end of this tube is the nozzle through which the vapour flows, which in order to obtain as sharply defined a beam of vapour as possible is made with an opening 0.1 mm. in diameter. The photographic plate is placed at right angles to the primary beam, about 20 cm. farther on (fig. 5). The high vacuum required in the apparatus is maintained by a steel diffusion pump. To prevent the vapour diffusing throughout the apparatus it is made to flow against the bottom of a condensing vessel full of liquid air. At the instant of exposure, which is controlled by a deviating

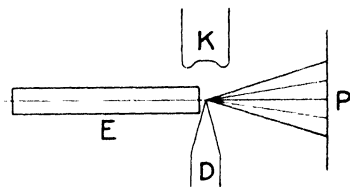


Fig. 5.—Diagram of the Apparatus

magnet worked by a clockwork relay, the vapour streams out from the supply vessel through the nozzle. As a rule, owing to the high vacuum in the apparatus, the vapour pressure of the substance at ordinary temperature is sufficient to give rise to an intense beam of vapour. Solid substances are vaporized in a small oven (such as is used in molecular-beam experiments), which at the moment of exposure is submitted to great pressure. The exposure is extremely short (1/10 sec.–1 sec.), and the interference rings of carbon tetrachloride are clearly shown on a fluorescent screen. In conclusion, we may add that this is the simplest form of electron diffraction experiment known at present and may easily be carried out in a chemical laboratory provided with high-tension apparatus.

The first experiments were made with carbon tetrachloride, which immediately gave the rings anticipated. The sixth and seventh maxima could actually be recognized in places. The electrons were accelerated by an electromotive force of 30–50 kilovolts, so that by equation (1) the de Broglie wave-length associated with them was 0.070–0.055 Å. In order that we may be able to make calculations from the photographs it is essential that the electromotive force should be accurately known; it was measured at the instant of exposure by a Starke-Schröder high-tension voltmeter, the instrument having previously been calibrated by measurements on electron diffraction photographs with gold foil. The carbon tetrachloride photographs in fig. 6 (see plate), were made with (a) 54-kilovolt electrons, and (b) 40-kilovolt electrons, and clearly indicate the variation with the wave-length.

If the regular tetrahedron is taken as the fundamental model for the tetrachlorides, there arises the possibility of determining the radius of the central atom. For if we replace the small carbon atom in CCl_4 by the larger silicon atom or the still larger titanium atom, the chlorine atoms situated at the corners of the tetrahedron must move farther and farther apart if tetrahedral symmetry is to be retained. In actual fact the diffraction rings for constant electromotive force are considerably smaller for TiCl_4 than for SiCl_4 and for SiCl_4 than for CCl_4 . For comparison with V. M. Goldschmidt's values for the radii, calculated from X-ray data, we quote the ionic radii, as the atomic radii given there apply only to the metallic state.* We assume a diminution of the distance between the atoms by 6 per cent for the passage from co-ordination number 6 to co-

* Personally communicated to me by Professor Goldschmidt.

ordination number 4, so that we obtain the values given in the top row of the table for the distances between the chlorine atoms. The values given in the bottom row, which were obtained by experiments on the vapour molecules, all exhibit a further diminution of one or two per cent; this perhaps indicates the existence of a slight contraction of the molecule due to polarization.

CCl ₄ in CCl ₄	SiCl ₄	GeCl ₄	TiCl ₄	SnCl ₄
According to Goldschmidt 2.97	3.38	3.45	3.76	3.92 Å
Experimental (± 0.03 Å) 2.96	3.28	3.34	3.60	3.90 Å

In the study of cyclic organic molecules we are in the first place interested in the difference of the distances between the carbon atoms in the aromatic and aliphatic bonds, and in the second place in the question whether finer differences in molecular structure, e.g. different space configurations of molecules, can be established. Molecules consisting of *one* kind of atom are obviously better suited to the investigation of the latter problem than those consisting of several kinds of atoms.

The distance between the carbon atoms for aromatic compounds has been measured in the case of the benzene molecule, which is assumed to be plane. The intensity formula is

$$I = 6K \psi_c^2 \left[1 + 2 \frac{\sin x}{x} + 2 \frac{\sin \sqrt{3}x}{\sqrt{3}x} + \frac{\sin 2x}{2x} \right].$$

Calculation gives the distance as 1.4 Å for the aromatic bond. Cyclopentane was selected for the determination of the interatomic distance in aliphatic compounds. The intensities calculated for the plane regular pentagon of Werner's strain theory are given in formula (5) above, and plotted in fig. 2. For the value of F in the expression for the scattering power of the carbon atom the value obtained for graphite from X-ray data (Lonsdale) was used in the case of benzene, and that for diamond (Brindley) in the case of cyclopentane. If the value for graphite is used in the latter case, we obtain a series of intensities which in addition to a small displacement of the position of the maxima exhibits a change in the relative intensities. The fact that this distribution of intensities does not agree so well with that obtained from the cyclopentane photographs as the former one leads us to believe, as we have already mentioned,

that the electronic configuration of the bond has an appreciable effect. In the aliphatic bond the distance between the carbon atoms turns out, apart from experimental errors, to be greater (1.5 \AA) than in the aromatic bond.

To establish the difference between the aromatic and aliphatic bonds we selected benzene and cyclopentane because in both cases the plane model may be regarded as established. The cyclohexane molecule, on the other hand, is certainly not plane (it exists in two forms, the "step" form and the "trough" form). Now the distributions of the intensities for the two forms of C_6H_{12} are not exactly the same, and apart from the effect of the atom form factor, differ from that for benzene. In actual fact the cyclohexane photographs, as compared with the benzene photographs, besides exhibiting interference rings of differing diameter, show a difference of the relative intensities corresponding to that required by the theoretical curve (the first ring being more intense in C_6H_{12} than in C_6H_6). But as the atom form factor also gives rise to a similar change in the behaviour of the intensities, nothing further can be presupposed with certainty, e.g. about the ratio of mixing of the two forms in cyclohexane.

A third problem is that of the free mobility required by chemical data. The mobility occurring in chains with single bonds is readily demonstrated, e.g. in 1-5-dichloropentane. From the above data we may deduce what diameter a ring may be expected to have if a rigid zig-zag configuration exists, i.e. if the two chlorine atoms are the greatest possible distance apart. The fact that the experimental result differs from this value indicates that the distance between the chlorine atoms is considerably altered, i.e. that mobility exists. This line of investigation has not been pursued further. The *cis-trans* isomerism in the case of a double bond may, as Debye has shown by means of X-ray diffraction photographs for *cis*- and *trans*-dichloro-ethylene vapour, be recognized by the differing distances between the chlorine atoms. In our electron diffraction experiments with *cis*- and *trans*-dichloro-ethylene we found that a trifling admixture of the other isomer appreciably altered the diffraction pattern and even the positions of the rings. While the diameters of the rings are approximately in the ratio of 5 : 9 for the pure substance (which indicates the trifling scattering effect of the C-Cl periods), if the two isomers are present in equal quantities the first ring moves into the neighbourhood of the second, the ratio being then about 5 : 7.5. The interference method of measuring the distances between the

atoms in 1-2-dichloro-ethane offers the possibility of investigating the free mobility about the single carbon bond. Thus it should be possible to establish whether the chlorine atoms in 1-2-dichloro-ethane take up any positions between two extreme limits (the *cis*- and *trans*-positions), or whether definite positions have the preference (limited mobility). The diagrams to be expected on theoretical grounds are widely different. The experimental result is best understood by assuming that in 1-2-dichloro-ethane there are two positions of equilibrium which occur about equally often. In fig. 7 (see plate), (b) is a 1-2-C₂H₄Cl₂ photograph, while (a) is a 1-1-C₂H₄Cl₂ photograph taken under the same conditions. This last photograph is meant to show that the superposition of the C-Cl periods has no essential influence on the scattering effect of the two chlorine atoms which in the solid state are attached to the same carbon atom, so that the diameters of the rings are in the ratio 5 : 9 : 13 required by the simple interference function. The above-mentioned observation for mixtures of *cis*- and *trans*-dichloro-ethylene makes the interpretation of our result for 1-2-dichloro-ethane by the existence of two isomers which are readily transformed into one another very plausible. Oxalyl chloride and 1-2-bromo-ethane give a similar arrangement of rings, the diameters of the rings in the latter case being smaller to correspond with the somewhat greater atomic radii and interatomic distances of the bromine atoms. We would emphasize, however, that these experiments merely give an *indication* of the existence of the two states of the substances, and not a proof.

5. Further Applications

In conclusion we shall mention some other problems which are meanwhile being attacked by these methods but about which nothing final can yet be stated. Experiments on the *ortho*, *meta*, and *para* di-substituted benzenes offer the possibility of establishing the small contractions caused in the benzene nucleus by the addition of heavy atoms, which are indicated by some anomalies in the dipole moments. In the case of chemical decomposition the question of the nature of the resulting fragments is of interest; attempts are made to determine, e.g. whether free or joined methyl groups are to be identified from their diffraction effects in the decomposition of lead tetramethyl. The mechanism of a homogeneous gas reaction may be investigated by bringing the primary beam of cathode rays to the point of intersection of two different beams of vapour, and the

existence of a product of reaction may be deduced from the diffraction pattern.

These problems, however, still await a clear-cut solution. I hope, however, that I have been able to show that important questions of structural chemistry can even at present be answered with some certainty and degree of accuracy by means of this method of Debye's for measuring the distances between the atoms of a molecule, a method which is not only easy to understand from a theoretical point of view, but also easy to carry out experimentally.

The Scattering of X-Rays and of Cathode Rays

H. MARK, LUDWIGSHAFEN AM RHEIN

In connexion with the two interesting experimental papers by Rupp and Wierl, I should like to attempt to give a concise outline of the way in which the theoretical treatment of interference phenomena with X-rays and electrons has been developed hitherto. I particularly wish to emphasize those points which eventually led to the adoption of the Darwin-Ewald dispersion theory of X-rays, in order to draw comparisons with the present position in the realm of electrons. This will perhaps make it clear to what extent we are meantime obliged in the case of electrons to accept Bethe's dispersion theory, and which experiments seem best adapted for testing the special results of this theory.

I.—THE SCATTERING OF X-RAYS

1. Laue's Theory of X-ray Interference

If we assume that all the lattice points of a crystal are excited in the same way by an incident wave and have no mutual effects on each other, we obtain, according to Laue, the following expression for the intensity of the X-rays scattered in the direction θ :

$$I(\theta) \sim \frac{|\psi|^2}{R^2} \frac{\sin^2 M_1 A_1}{\sin^2 A_1/2} \frac{\sin^2 M_2 A_2}{\sin^2 A_2/2} \frac{\sin^2 M_3 A_3}{\sin^2 A_3/2}, \quad (1)$$

where A_1, A_2, A_3 are given by

$$A_1 = \frac{2\pi}{\lambda} a_1 (\alpha - \alpha_0)$$

$$A_2 = \frac{2\pi}{\lambda} a_2 (\beta - \beta_0)$$

$$A_3 = \frac{2\pi}{\lambda} a_3 (\gamma - \gamma_0);$$

M_1, M_2, M_3 are the numbers of lattice points in the directions x, y, z ; a_1, a_2, a_3 are the periods of the spacing in these directions; $\alpha_0, \beta_0, \gamma_0$, and α, β, γ are the direction cosines of the incident and reflected rays; λ is the wave-length of the X-rays used; and ψ is the scattering amplitude of the individual atom and depends on the particular distribution of charge. Here and in what follows, however, we shall not take this latter effect into account, as it is discussed in greater detail in the paper by Mott (p. 41). The expression (1) has maxima of infinite height at the points where

$$\left. \begin{aligned} a_1(\alpha - \alpha_0) &= h\lambda \\ a_2(\beta - \beta_0) &= k\lambda \\ a_3(\gamma - \gamma_0) &= l\lambda \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Thus equation (1) gives us no information about the intensity of the scattered radiation, as is also obvious from the fact that this intensity increases in proportion to the square of N , the number of particles causing the scattering, so that by suitable choice of the crystal it could be made to exceed the primary intensity.

This unsatisfactory feature of the kinematic theory of interference from the theoretical point of view was pointed out by Laue himself and formed the first incentive to further development. Bragg's law of reflection and Polanyi's layer line relationship are special cases of Laue's general equations (2). The former, without saying anything about the intensity, states that when light of wave-length λ is reflected at a series of planes at distance d apart the angle θ between the primary ray and the reflected ray is determined by the equation

$$\xi_0 = \sin \frac{\theta}{2} = \frac{\lambda}{2d} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus if a single crystal is rotated in a monochromatic beam of X-rays an intense line will be obtained at one moment, while at the next moment the intensity will be zero; this is shown diagrammatically in fig. 1, in which the reflected intensity is taken as ordinate and the quantity

$$\xi = (\chi - \chi_0) \sin \chi$$

as abscissa, where χ_0 is Bragg's glancing angle, i.e.

$$\chi_0 = \frac{\theta_0}{2}.$$

According to this figure reflection on the elementary theory is infinitely sharp; nothing is said about the intensity. Apart from intensity problems, which raise theoretical difficulties, Laue's theory reproduces the experimental relationships very well for X-rays, and it was only when very accurate measurements were made in Siegbahn's laboratory that an extension was called for from the experimental side.

2. The Formal Introduction of a Refractive Index

Siegbahn and Stenström found, in fact, that no absolutely constant value for d results if we calculate the distance between the planes from several orders of reflection. They interpreted their experimental results by introducing a formal refractive index μ , which causes the line to be displaced so that it no longer passes through the point $\xi = \xi_0$, and which differs from unity by about 10^{-5} to 10^{-6} . Here again,

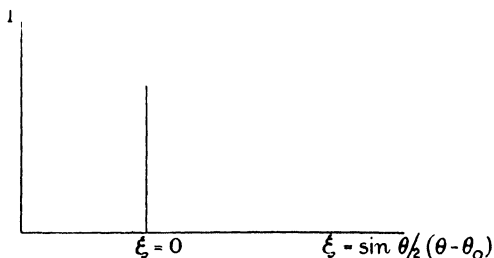


Fig. 1

nothing is said about the intensity or the separation; the diagram corresponding to fig. 1 merely shows the line displaced

into a position where it does not pass through ξ_0 (see fig. 2). This treatment bears a certain analogy to the formal introduction of the internal lattice potential in the reflection of electrons, and in the case of X-rays was very speedily abandoned in favour of the dispersion theory.

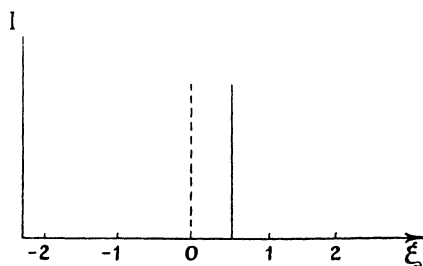


Fig. 2

3. The Dispersion Theory of X-Rays

Even before the experiments of Siegbahn and Stenström had necessitated an extension of the kinematic theory, the intensity problems referred to above had led Darwin, and subsequently Ewald, to calculate out the actual mutual effects of the dipoles existing and capable of vibration within a crystal. Starting with

very different assumptions, they nevertheless obtained results which are substantially in agreement. Ewald's method makes the relationships particularly clear and simple. He begins by investigating what field will produce a tentative dipole wave in a lattice (i.e. one of undetermined phase velocity) and expands this in terms of the contributions of the individual planes of the set. He then inserts these field intensities as the exciting forces in the vibration equations of the dipole, and thus obtains a system of homogeneous linear equations, which have no solution unless the determinant of their coefficients vanishes. Equating this determinant to zero, he obtains the phase velocity of the primary dipole vibration, which was left undetermined. In this way he ensures that the dipole wave

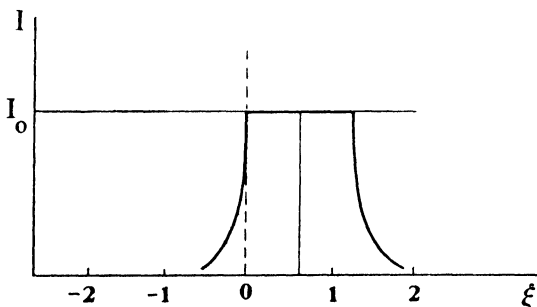


Fig. 3

is not *disturbed* by its own field, but *maintained* by it. In order to make comparisons with experiment it is also necessary to discuss the behaviour at the edge of a crystal in detail, as well as the limitation to only a few interference bands. The result for

the case of Bragg reflection at a lattice plane is illustrated by fig. 3 and is to the following effect:

It is not only the primary ray of intensity I_0 incident at the exact Bragg angle χ_0 that is reflected by the crystal surface: in addition there is an assemblage of incident rays adjacent to it on the side of positive ξ -values, which in spite of their incorrect angle of incidence give the same yield on reflection by the lattice plane as the "exact ray" does. With the assumptions made by Ewald—no temperature effect, constant atom form factor, and no absorption—the yield is 100 per cent, i.e. there is total reflection. The breadth of this region of total reflection (δ) may also be called the resonance breadth of the excited lattice vibration with respect to the incident ray; even slightly inaccurate excitation sets the crystal in the same state of vibration as exact excitation does. The fall of this resonance curve to either side is reproduced in an idealized form by Ewald; more accurate details of its form cannot be given in the first instance. In terms of the "reciprocal" lattice this result means that the

sphere of propagation has a definite thickness, so that, even if the excitation is somewhat inaccurate, points still fall within the spherical shell associated with it, and can thus be reflected.

To begin with, we see at once from fig. 3 that this theory reproduces the deviations from Bragg's law of reflection which are obtained experimentally. For if we consider the centre line of the reflected lines we see that it fails to correspond to Bragg's angle, just as is required by the experiments of Siegbahn and Stenström. The order of magnitude is also right; according to theory, the breadth of the region of total reflection comes to about 10" for light crystals and X-rays of medium hardness. Some more accurate values are given in Table I.

TABLE I
Breadth of the Region of Total Reflection

Substance.	Plane.	Measured breadth.	Breadth calculated by the dispersion theory.
Zinc blende	111	6.5"	7.0"
Diamond	111	5.5"	4.1"
Pyrites	100	8.5"	8.0"

In addition to removing an experimental difficulty which then existed, however, the theory has led to a number of predictions about the intensity and the breadth of the lines, which in subsequent years have been verified experimentally in various ways.

On the dispersion theory, the intensity of the interference bands is obtained from the breadth of the region of total reflection; according to Ewald, the theory yields the result that the intensity is proportional to the structure factor (the number of atoms causing the diffraction) and not, as in the kinematic theory, proportional to its square. The experimental verification of this result would require that ideal crystals should be available, whereas it is well known from experiments that most natural and artificial crystals consist of many small lattice blocks slightly displaced with respect to one another, so that the dynamical argument can only be applied to one of these blocks by itself. The whole crystal must be treated as a mosaic of such blocks, and the calculation of the intensity, which was carried out first by Darwin and subsequently in more detail by Waller, represents a combination of the dispersion theory and the kinematic theory.

In order to test the dispersion theory *per se* the intensities of numerous reflections were measured by W. H. Bragg, Ehrenberg, Ewald, and others, for as ideal diamonds as could be got and for zinc blende. It turned out that the relationships actually *are* better reproduced if the intensity is taken as proportional to the structure factor S than if it is taken as proportional to the square of the structure factor. A proposal by W. L. Bragg that in mosaic crystals the reflected intensity ρ should be taken as proportional to

$$\frac{|S|^2}{\mu + a\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

(μ being the true coefficient of absorption, and a a constant) has been adopted in practical measurements of X-ray intensity. For great intensities ($a\rho \gg \mu$; strong extinction and internal mutual action) we obtain the relationships given by the dispersion theory, while for small intensities ($a\rho \ll \mu$; i.e. slight mutual action) we obtain the simple relationships given by the kinematic theory.

All these considerations refer to the intensity of strong beams, i.e. such as result from direct interference with the primary beam. In principle, however, the theory is also capable of predicting the existence of "weak" interferences which may arise from the primary beam passing over a strong interference beam. This mutual action of three beams has been explicitly worked out for certain cases by Ewald and G. Mayer; it is related to the secondary spectra in X-ray photographs. Bethe has indicated the possibility that the forbidden reflections in the diamond diagram (222) and (622) may arise dynamically in this way from the intense interferences (111) and (311). This, indeed, is a natural idea, as the "forbidden" reflections have hitherto been obtained only in the case of diamond, which is known to approach the ideal crystal particularly closely. To test this, investigations were made whether the forbidden reflections vanish when quite hard rays are used or decrease in intensity when particularly fine diamond powder is used. According to the dynamic theory both these phenomena should occur, because both processes reduce the extinction and hence the magnitude of the mutual dynamical effects. Experiments have hitherto yielded a decrease in the intensity of these interferences relative to (111), but the possibility of other explanations has not yet been so thoroughly excluded that we can safely assume the dynamical origin of the two forbidden interferences.

A whole series of experiments have been carried out to determine

the breadth of the resonance region directly. To begin with, Berger-Davis showed that for pyrites and calcite the order of magnitude comes out right. To intensify the effect he made use of the method of unsymmetric reflection and was able to confirm the results of Siegbahn and Stenström. More accurate measurements were subsequently carried out by Ehrenberg and Susich with a double spectrometer. They also succeeded in quantitatively establishing the relationship required by theory between the breadth of the region of total reflection and the angle of deviation. The dispersion theory, in fact, requires that the resonance region should become narrower as we pass to higher orders. This means that lattice planes which are not so densely packed with atoms have less capacity for reflecting primary beams which are incident at the wrong angle. The breadth of the region of total reflection, i.e. the deviation of the refractive index from unity, is smaller, so that the intensity of the reflected beam decreases and the separation increases. Both these statements agree qualitatively with experiment. We see, therefore, that with this degree of approximation it is meaningless to regard the refractive index as a constant depending on the material when X-rays are used, as it varies very rapidly with the direction relative to the lattice. The diminution in the region of reflection has been quantitatively established by means of experiments with the double spectrometer. Table II shows that these measurements are in good agreement with the theoretical results.

The absolute value of δ and its relationship to the atomic number are also facts which force us to assume the truth of the dispersion theory apart from considerations of the formal refractive index.

TABLE II

Interference with Aluminium Foil; $a = 4.06 \text{ \AA}$

λ for cathode rays = 0.07 \AA (equivalent to 30,000 V)

λ for X-rays = 1.54 \AA (Cu $K\alpha$)

Indices of Lattice Plane.	Sin $\theta/2$.			
	X-rays.		Cathode Rays.	
	Calculation.	Experiment.	Calculation.	Experiment.
111	0.330	0.332	0.0298	0.0298
200	0.380	0.378	0.0344	0.0338
220	0.538	0.534	0.0486	0.0493
311	0.627	0.630	0.0571	0.0565
222	0.656	0.655	0.0597	0.0608
400	0.760	0.757	0.0688	0.0679

The variation of δ with wave-length has also been much investigated, and *anomalous dispersion* has definitely been found to exist; a natural modification of the classical dispersion theory enables us to account for the latter. But since (according to Davisson and Germer) very few facts about these anomalous phenomena are meanwhile available in the case of electron reflection, we shall not trouble to describe these experiments.

4. Refinements of the Dispersion Theory

The Darwin-Ewald dispersion theory involves several idealizing assumptions. It does not take account of

- (1) the temperature effect;
- (2) the atom form factor;
- (3) inelastic collisions (Compton effect, photo-electric effect, Raman effect).

An extension of the theory in which the effect of temperature is taken into account is due to J. Waller. Calculation shows that to

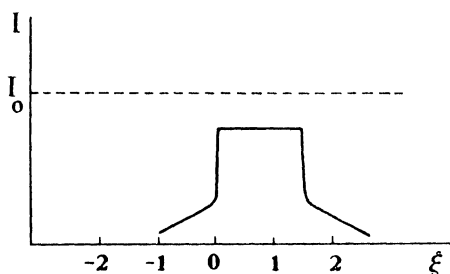


Fig. 4

a first approximation the breadth of the region of total reflection remains the same and only its height decreases with rise of temperature. Thus we no longer have total reflection; what happens is that part of the intensity previously concentrated in the interference beam is now distributed as

diffuse Debye radiation in all directions. This does not change the separation. This is in agreement with the elementary Debye theory of the temperature effect, which gives no broadening of the lines.

To a second approximation—in which the anharmonic vibration terms and the heat waves traversing the crystal are taken into account—there results a feeble concentration of the diffuse radiation in the neighbourhood of the interference maximum, i.e. a broadening of the base of the reflection diagram in fig. 4.

The effect of temperature on the intensity was investigated in Bragg's laboratory by James and his co-workers, and agreement with theory was obtained. Exact measurements to show that the loss of intensity does actually take place without an alteration in

the breadth of reflection are not yet available. Measurements which would enable the frequently-observed appendages to the interference maxima, resembling the base-mouldings of a column, to be definitely ascribed to the effects of temperature are likewise wanting.

It has not yet been found possible to work the atom form factor into the dynamic theory. To a first approximation it would probably have an effect similar to that of temperature, for in both cases we have to take account of the fact that the centres of diffraction are not points but have definite dimensions in space.

Inelastic collisions are dealt with in a very detailed paper by Prins which has only just appeared, in which the coherent scattered waves starting from the atoms are given a phase displacement as compared with the primary

wave. This phase displacement is chosen in such a way that by interference the scattered waves weaken the primary wave traversing them to the exact extent required by the absorption coefficient. The deviation of the refractive index from unity also enters into this in a complicated way. With certain assumptions about

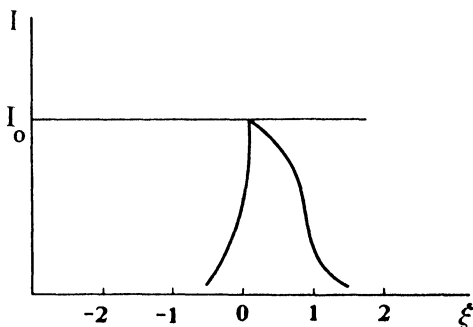


Fig. 5

the magnitude of the phase displacement in different directions the calculation gives the resonance curve shown in fig. 5. Its height and breadth half-way up are both altered, the intensity being diminished while the separation is increased by absorption. This is right, because absorption causes a decrease in the extent of the mutual dynamic effects. Experimentally only very few data giving the breadth of the lines on either side of an absorption region are available. With reference to the testing of Prins' calculation it would assuredly be of interest if such experiments were carried out more accurately by means of the double spectrometer.

To sum up, then, we may make the following statements. In the case of X-rays the kinematic theory represents a very good approximation to the actual relationships, so long as we are concerned merely with the reproduction of the positions of the interference bands, the deviations from experiment being of the order

of 10^{-5} . Intensity questions cannot be dealt with in this way. The calculations according to the dispersion theory have been carried out for two rays with the necessary refinements—except for the atom form factor. Experimental verification is generally hindered by the existence of mosaic structure. All the foregoing measurements taken together, however, clearly indicate that the predictions of this theory are also justified quantitatively. To round the matter off, it would be desirable to carry out experiments (especially with the double spectrometer) on the relationship between the change in breadth of the interference band and the temperature or the absorption.

II.—ELECTRON DIFFRACTION IN CRYSTALS

1. De Broglie's Theory of Electronic Interference

In order to subject the diffraction of electrons by crystal lattices to calculation, it is natural to begin by combining the simple de Broglie equation

$$\lambda = \frac{h}{mv} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

with Laue's equations or with Bragg's law of reflection. This very natural combination was applied in all the calculations and for fast electrons gives remarkably good agreement with the results of X-ray experiments. In Table II, for example, we gave the glancing angles of several planes in the aluminium lattice for X-rays and for cathode rays, and beside them the values calculated from Bragg's law of reflection and de Broglie's equation, using the wave-lengths $\lambda_1 = 1.54 \text{ \AA}$, $\lambda_2 = 0.14 \text{ \AA}$. We see that in both cases the results of experiment are excellently reproduced using the same spacing $a = 4.06 \text{ \AA}$. Numerous experiments by Kikuchi, Ponte, Rupp, Thomson, and Wierl with fast electrons ($V > 15,000$ volts) have justified this method, though of course it must be emphasized that the accuracy here is far short of that obtained with X-rays. In the case of X-rays the centre of an interference band can be determined by means of Siegbahn's precision methods to 5 or 6 places under suitable conditions, and even to 7 places if the conditions are particularly favourable, whereas in the case of fast electrons no more than 3 places can be obtained even from Wierl's best photographs. Within this range of accuracy, however, the elementary theory of interference is in agreement with experiments on *fast* electrons.

2. The Formal Introduction of a Refractive Index

Even Davisson and Germer's first work on the reflection of *slow* electrons by crystal lattices made it clear that the facts could not be accurately represented by equations (3) and (5); on the contrary, definite deviations from Bragg's law of reflection occur. These were first explained by Patterson as being due to a diminution of the distance between the lattice planes at the surface. Bethe has shown, however, that better agreement with experiment is obtained by expressing the action of the crystal on the electrons by means of a mean lattice potential V_0 . Schrödinger's equation for the de Broglie waves with an internal lattice potential is then

$$\Delta \psi + \frac{8\pi^2 m}{h^2} (E - V_0) \psi = 0. \quad . \quad . \quad . \quad (6)$$

On solving this equation we obtain, instead of de Broglie's equation for free electrons, the equation

$$\lambda = \sqrt{\frac{h^2}{2me(E + V_0)}} \quad . \quad . \quad . \quad (7)$$

which on comparison with (5) gives a refractive index of magnitude

$$\mu = \sqrt{1 + \frac{V_0}{E}} \quad . \quad . \quad . \quad (8)$$

To this degree of approximation the refractive index may be regarded as a constant depending on the material and independent of direction; it results in a displacement of the lines from the positions determined by Bragg's law and is completely analogous to the Siegbahn-Stenström index of refraction for X-rays. In contradistinction to the X-ray case, however, the refractive index for electron diffraction deviates very considerably from unity for *slow* electrons. According to Bethe, the internal lattice potential for nickel as calculated from Davisson and Germer's experiments comes to about 15 volts. From equation (8) we see immediately what effect this has on electrons of different velocities. In Table III some values of the refractive index calculated in this way are given for electrons of different velocities in the case of nickel. We see from them that with very fast electrons, i.e. electrons of over 30,000 volts, the deviations from the kinematic theory of interference become small, although they are still a thousand times greater than in the case of X-rays of medium wave-length. With slow electrons the

deviations are very considerable and give rise to important modifications in the general appearance of the phenomena.

TABLE III

μ	Velocity of the electrons in "volts".	Corresponding X-ray wave-length.
4	1	12.2 Å
1.58	10	3.88 Å
1.07	100	1.22 Å
1.01	1000	0.39 Å

3. The Dispersion Theory of Electron Diffraction

Immediately after the introduction of a constant refractive index Bethe developed a dispersion theory of electron diffraction which is very closely related to the Darwin-Ewald theory. In this theory the propagation of de Broglie waves through a crystal is investigated, the potential being expanded in a triple Fourier series in terms of the contributions of the individual lattice planes hkl . Thus V_0 in Schrödinger's equation is replaced by a triple Fourier series with the coefficients V_{hkl} . In accordance with this assumption, the solution is also taken as having the form of a Fourier series in terms of the individual lattice planes; as a possible mode of propagation of de Broglie waves we obtain, as in the case of X-rays, an elementary interference field, i.e. a whole set of plane waves whose directions of advance are those of all possible reflections and whose intensities are very closely related to each other by the vibration equations.

In the case of two beams Bethe obtains the following result. The intensity of the secondary beam does not merely depend on the direction of the primary beam, i.e. on the inaccuracy of the excitation, but under certain circumstances the other feeble beams may add to it appreciably. The ψ -functions of the beams are multiplied by the higher lattice potentials, so that the latter have an effect on the intensity, and, conversely, may theoretically be determined by measurements of intensity. For very fast electrons, i.e. when the refractive index is very small or the spherical shell of propagation very thin, the number of the weak reflections falling within the shell is not large, and the effect of these additional terms on the intensity of the reflected beam vanishes as compared with the intensity directly split off from the primary beam. Theory shows that the existence

of this effect of the additional terms could only be established by extremely accurate measurements, and in practice it is doubtless completely masked by other effects due to change of temperature, the atom form factor, inelastic collisions, &c. For slow electrons the lattice points of many feebly reflected planes in the reciprocal lattice lie within the shell of propagation and the effect of the higher coefficients in the expansion of the lattice potential is considerably greater. Experimental confirmation of this effect would be of extreme importance as a test of the theory.

Now Laue, by considering the relationships at the surface in detail, has indicated that the sudden breaking off of the lattice potential at the boundary of the crystal in Bethe's theory represents a considerable idealization of the actual state of affairs. According to Laue, the potential decreases outwards in a complicated way, and in the case of slow electrons with slight penetrating powers we must remember throughout that the relationships are greatly affected by this external potential. Thus slow electrons do not seem particularly suitable for a test of Bethe's theory. For this reason it seemed advisable to use electrons of moderate velocity in testing the dispersion theory. From theory, for example, we find that electrons of 2000 volts penetrate through about 30–50 lattice planes into the crystal. Here the deviation of the refractive index from unity comes to about two parts per thousand and the separation is accordingly 500 to 1000. Seeing that the electrons penetrate so far into the crystal we may suppose that the effect of the 50 successive lattice planes preponderates over that of the surface potential to such an extent that the latter may be neglected. On the other hand, with electrons of medium velocity those effects which distinguish Bethe's theory from that with a medium lattice potential become relatively small, and the question arises, can we obtain a velocity for which Laue's considerations are no longer of serious moment but for which the phenomena peculiar to the dispersion theory are still within the reach of experiment? We shall consider this question for each of the phenomena predicted by the theory in turn.

(a) *The Separation.*—In theory both the absolute value of the separation and its relationship to the order can be determined by direct measurement of the breadth of the bands, provided the primary beam of electrons is sufficiently homogeneous.

The velocity spectrum of thermionic electrons may be carried down to about 1/10 volt by means of a Hertz equipotential cathode.

If the electrons are accelerated by means of a 2000-volt battery of accumulators, we can reckon on a "natural breadth of band" of 10^{-4} . According to Table IV this would suffice for a determination of the separation for the first order, but not for a verification of the decrease of the breadth of the band for higher orders. The primary breadth of the band may, however, easily be divided by ten by means of a magnetic field, so that no difficulties may be expected in this direction. K. Wolf has begun experiments on these lines, though he has not yet used velocities sufficiently great to be independent of Laue's considerations or of general surface con-

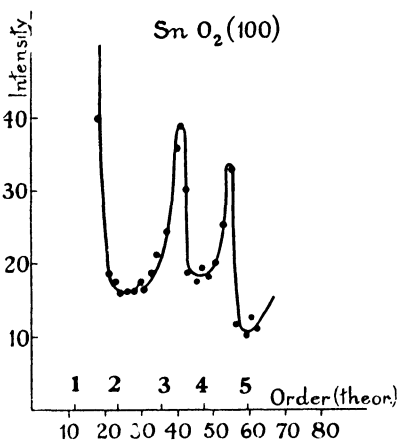


Fig. 6

ditions—a gaseous layer, layer of oxide, or other contamination. So far his experiments have led to no clear-cut conception of the phenomena. Although the curves are in good agreement among themselves as regards the position of the maxima, both for variations in the angle and in the electromotive force, he obtained quite unexpected intensity effects and deviations from the anticipated positions which are difficult to explain. Fig. 6 may serve as an example of this. It shows the reflection of electrons at the (100) plane of SnO_2 for glancing

angles between 0° and about 30° . This reflection has been tested by repeated experiment with various electromotive forces and found to be reproducible. The large maxima are presumably to be ascribed to the fourth and fifth orders of (100). But with a refractive index constant for all orders no consistent indices are obtained.

(b) *The Intensities*.—According to Bethe's theory the intensities for fast electrons are calculated from the initial term only of the series for the lattice potential. This calculation therefore corresponds to that of the atom form factor in the reflection of X-rays. Bethe has shown how one quantity may be expressed in terms of the other, and we see from fig. 3 of Wierl's paper (p. 18) that this calculation receives excellent confirmation from experiment. For slower electrons, however, the fall of intensity of the higher orders can no longer

be described by a simple atom form factor, i.e. by a single lattice potential, but the higher terms of the series come in, and under certain circumstances may suppress one particular order and intensify the next. K. Wolf has, in fact, found anomalies of this kind in the intensity, feeble lower orders being frequently observed next to strong higher orders. But it is not worth while comparing these experiments quantitatively with theory either, because the velocity of the electrons used in them is never large enough to guarantee independence of surface properties.

(c) *The Forbidden Reflections*.—Owing to the greater thickness of the shell of propagation, with sufficiently slow electrons forbidden reflections may be expected to occur when they can arise from a strong lower order. This is the case e.g. for the (222) and (622) planes in diamond, just as with X-rays. K. Wolf caused 335-volt electrons to be reflected at the octahedral plane of diamond. The curve exhibits a maximum which may be identified with (222). According to this interpretation the intensity ratio (222):(111) would be considerably greater than that observed for X-rays. This assumption is also to be made with caution, owing to the somewhat small velocity of the electrons used; the experiment will have to be repeated with faster electrons.

4. The Consideration of Inelastic Collisions

Inelastic collisions have also been dealt with recently in a detailed paper by Bethe. The results, however, refer only to fast electrons and to the diffraction caused by a single atom. The continuous background formed by the electrons which are scattered inelastically falls off much more steeply, according to this theory, than the coherently scattered de Broglie waves. Thus when the angle of deviation is large we are more or less in a position to neglect it in experiments.

Hitherto no experiments are available which would serve as a quantitative verification of the results contained in Bethe's paper.

The Atom Form Factor

N. F. MOTT, MANCHESTER

If a beam of electrons falls on a free atom, the intensity of the beam scattered through an angle θ is, at a distance r from the scattering atom,

$$\frac{1}{r^2} \frac{\epsilon^4}{4m^2v^4} (Z - F)^2 \operatorname{cosec}^4 \frac{1}{2} \theta \quad . \quad . \quad . \quad (1)$$

times the intensity of the original beam. ϵ is here the charge on the electron, m its mass, and v the velocity of the beam. Z is the atomic number of the scattering atom, and F , a function of θ , is the atomic scattering factor, which will be defined below. The corresponding formula for unpolarized X-rays is

$$\frac{1}{r^2} \frac{\epsilon^4}{m^2c^4} F^2 \frac{1 + \cos^2 \theta}{2} \quad . \quad . \quad . \quad (2)$$

I wish in this paper to discuss the derivation of these two formulæ, and to make as "anschaulich" as possible the connexion between them. I wish also to discuss under what conditions the approximations used in deriving formula (1) are valid.

I would first emphasize that the formula (1) is derived for free atoms. There are three reasons why the scattering factor may be different for atoms bound in a crystal. Firstly, there is a potential jump, usually of the order of 10 volts, at the crystal surface. This will cause a refraction of the electron beam. Secondly, the wave scattered from any atom may be scattered again by another atom. Neither of these disturbing factors will greatly affect the scattered intensity for electrons of energy above, say, 2000 volts.* Thirdly, the atoms in the crystal may be deformed or ionized by the neighbouring atoms. This third cause will be discussed later.

I will now derive the formulæ (1) and (2). We imagine the atom to behave as a static distribution of electric charge, of density

* Cf. Bethe, *Ann. d. Physik*, **87**, 55 (1928).

$\epsilon |\psi(x, y, z)|^2$ at any point. ψ is the approximate wave function worked out by the method of Hartree. Results obtained using this model of the atom are only valid for electrons of energy considerably greater than the ionization energy of the atom used.

In deriving the formula (2) for X-rays we assume that each element of charge $d\rho$ in the atom scatters a wavelet of amplitude

$$\frac{1}{r} \frac{\epsilon}{mc^2} d\rho \cdot \sin \phi \quad . \quad . \quad . \quad . \quad . \quad (3)$$

times that of the incident wave, according to the classical formula of J. J. Thomson. ϕ is here the angle between the electric vector of the incident light and the direction of scattering. We assume further that the wave fronts inside the atom are very little distorted by refraction, an assumption that is justified by the fact that ϵ^2/mc^2 is a length very much smaller than the radius of the atom. Then each little wavelet starts out with known phase, namely that of the incident wave. Considering the interference of all these wavelets, and also averaging over all polarizations of the incident wave, we obtain the formula (2), where

$$F = F(\theta) = 4\pi \int_0^\infty \frac{\sin \mu r}{\mu r} |\psi(r)|^2 r^2 dr \quad . \quad . \quad . \quad (4)$$

$$\mu = 4\pi \sin \frac{1}{2} \theta / \lambda.$$

λ is the wave-length of the waves.

In deriving the formula (1), we assume, analogously, that each element of charge scatters a wavelet of amplitude

$$\frac{1}{r} \frac{\epsilon d\rho}{2mv^2} \operatorname{cosec}^2 \frac{1}{2} \theta. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This formula is equivalent to the Rutherford scattering formula, and can be justified on the wave mechanics.* We assume as before that the wave fronts are not distorted in the atom, which will only be the case if ϵ^2/mv^2 is small compared to the radius of the atom, that is to say, for fast electrons. Considering the interference of these wavelets, we obtain a wave of amplitude

$$\frac{1}{r} \frac{\epsilon^2}{2mv^2} F \operatorname{cosec}^2 \frac{1}{2} \theta.$$

Now in formula (5) ϵ and m refer to the charge and mass of

* Cf. Gordon, *Zeitschr. f. Physik*, **48**, 180 (1928).

the incident particle, not, as in (3), to the atomic electron. Therefore the wave scattered by the nucleus, negligible for X-rays, is here of importance. The amplitude of this wave is

$$\frac{1}{r} \frac{Z\epsilon^2}{2mv^2} \operatorname{cosec}^2 \frac{1}{2} \theta,$$

and the phase is clearly opposite to that of the wave scattered by the electrons. Therefore the amplitude of the total scattered wave is

$$\frac{1}{r} \frac{\epsilon^2}{2mv^2} (Z - F) \operatorname{cosec}^2 \frac{1}{2} \theta, \quad . \quad . \quad . \quad (6)$$

which yields the formula (1).

The formula is in fair agreement with the experiments of Dymond on scattering in a gas (helium) and with the experiments of Mark and Wierl with thin metallic foils.

It is interesting that the function (6) is a function of $\sin \frac{1}{2}\theta/\lambda$. For a neutral atom, as $\sin \frac{1}{2}\theta/\lambda$ decreases, the scattered intensity increases steadily, and tends to a finite value. For a positively ionized atom, the scattered intensity tends to infinity. For a negatively ionized atom the scattered intensity rises to a maximum, falls to zero, and then rises to infinity as $\theta \rightarrow 0$.

It is not, however, possible to find out whether atoms in a metal are ionized or not by this method; the F curves for the neutral and for the ionized atom differ only for small values of $\sin \frac{1}{2}\theta/\lambda$ and the first spectrum is always found at too large a value for the difference to be observable. The reason for this is that the orbits of the valence electrons undisturbed are so big that in a metal they would overlap, and the charge distribution that they would produce in a metal is not very far from uniform. Thus the intensity of the observed spectra cannot be appreciably affected by these electrons.

As well as the coherent scattering, which has the same wave-length as the incident waves, an atom scatters waves of reduced wave-length. The intensity of these waves is not included in the formulæ (1) and (2). For X-rays falling on a hydrogen atom, the total intensity scattered inelastically, due both to Raman effect and Compton effect, is given by the formula

$$\frac{1}{r^2} \frac{\epsilon^4}{m^2 c^4} (1 - F^2) \frac{1 + \cos^2 \theta}{2} \quad . \quad . \quad . \quad (7)$$

It is seen that the total scattered intensity, elastic and inelastic,

is given by the Thomson formula, assuming that the waves scattered from different parts of the atom do not interfere.

The equivalent formula for electrons, given by Bethe,* is

$$\frac{1}{r^2} \frac{e^4}{4m^2v^4} (1 - F^2) \operatorname{cosec}^4 \frac{1}{2} \theta. \quad . \quad . \quad . \quad (8)$$

For atoms containing more than one electron, we must find F for each electron separately, and sum (7) or (8) over all the electrons. The scattered intensity thus obtained includes that derived from inelastic collisions forbidden by the exclusion principle; the intensities due to these must be calculated, and subtracted. Further details are given in Bethe's paper.

* *Ann. d. Physik*, **5**, 305 (1930).

The Effect of Temperature on the Electrical and Thermal Resistance of Metals in Theory and Experiment

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In recent years the electron theory of metals has received a new lease of life through the introduction of the Fermi statistics and of the idea that the resistance of the electrons in the metal arises from the scattering of the electron waves in the lattice of atomic ions. A fairly large number of papers have appeared in which some difficulties in the assumptions of the older electron theory, e.g. the problems of the specific heat of the electrons, of the motion of free electrons in the strong fields of force of atomic ions, &c., seem to have been satisfactorily solved.* Yet it is not easy for the outsider to form an opinion about the success of these new theories in practice. This is only partly due to the considerable amount of mathematics which seems to be required if we are to penetrate deeply into the essential nature of metallic conduction with any degree of strictness. A further obstacle lies in the fact that owing to the mathematical difficulties the new theories are necessarily confined to first approximations, which may indeed enable us to calculate the order of magnitude of the specific resistance, the temperature law for the limiting cases of high and low temperatures, &c., but which are incapable of supplying any satisfactory answer to the question why one metal conducts better than another, or what the temperature law is in the intermediate region, much less how the phenomena of superconduction are to be interpreted quantitatively.

Hence it is clear that in the comparison between theory and experiment, on which I consider it desirable that a discussion of

* Cf. A. Sommerfeld, *Zeitschr. f. Physik*, **47**, 1 (1928); W. V. Houston, *Zeitschr. f. Physik*, **48**, 449 (1928); *Phys. Rev.*, **34**, 279 (1928); J. Frenkel and N. Mirolubow, *Zeitschr. f. Physik*, **49**, 885 (1928); F. Bloch, *Zeitschr. f. Physik*, **52**, 555 (1928); **59**, 208 (1930); R. Peierls, *Ann. d. Physik*, **4**, 121 (1930); **5**, 244 (1930).

the modern theories should be based, it will not be advisable to make claims of too sweeping a nature. Yet it must be possible to come to some decision when the differences are so marked as those which have been obtained theoretically, e.g. for the limiting law of electrical resistance at low temperatures (proportional to T^2 , T^3 , T^4 , and T^5).

Experimentally the effect of temperature on electrical resistance may be established with comparative ease and accuracy. To some extent, also, this law has a universal character, being dependent on few parameters. Hence it seems particularly well suited to the testing of the theories, at least so far as the mutual action of electrons and the lattice of atomic ions is concerned. On this occasion, therefore, I shall chiefly confine myself to the problem of the effect of temperature on the electrical resistance,* with some remarks about the thermal resistance.

The Temperature Law of Electrical Resistance

1. Among the modern theories that of Bloch† aroused my special interest when he showed that it leads to a T^5 law for the specific resistance ρ . For recent experiments with very pure metals ‡ indicate that the empirical law $\rho \sim TC$ (C is the atomic heat, i.e. in the limit $\rho \sim T^4$) falls away too slowly at very low temperatures. Not only were the values of Θ to be substituted in Debye's function C greater by a few per cent than those required to represent the atomic heat, but it was also possible to show that the behaviour of the resistance apparently required that Θ should increase as the temperature fell.§ Further, Bloch himself adduced a very striking confirmation of his theory in the case of gold, being successful in calculating the ratio of the resistances in the T and T^5 regions.

Unfortunately, however, it was not possible to test Bloch's theory in the intermediate region, as there he thought a temperature function could not be defined.

On the other hand, it seemed to me that there must be a grain of truth in the empirical relationship $\rho \sim TC$, seeing that it works so remarkably well for medium temperatures. I therefore returned to the only theoretical deduction of this relationship which I know

* See also G. Borelius, *Zeitschr. f. Physik*, **54**, 806 (1929).

† F. Bloch, *loc. cit.*

‡ Especially the measurements by Meissner down to the temperature of liquid helium.

E. Grüneisen, *Zeitschr. f. Physik*, **46**, 151 (1927).

of, namely, that by L. Brillouin,* and attempted to introduce into it the idea of Bloch, hitherto disregarded, that the exchange of energy between elastic waves and electron waves must take place in quanta $h\nu$ of the elastic vibrations, i.e. must decrease as the temperature falls, for of course even at low temperatures it is only the lower frequencies that carry energy capable of being exchanged. In this way I obtained a law which, on the one hand, is found to coincide with an integral which appears in Bloch's theory as an approximation for low temperatures, but which, on the other hand, is capable of representing the resistance for the whole range of temperature, as far as may be expected of any law.

2. L. Brillouin* obtains a theoretical basis for the empirical law $\rho \sim TC$ in the following way. Starting from a paper by Einstein and Hopf,† he considers the light pressure which acts on a material particle moving with velocity v through an isotropic field of black radiation of energy density $E(\nu)d\nu d\omega$ (for the frequencies ν to $\nu + d\nu$ and the solid angle $d\omega$) with the absorptive power or scattering power $\alpha(\nu)$. There results a force

$$f = -Rv, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$R = \frac{4\pi}{c} \int \alpha(\nu) \left[E(\nu) - \frac{\nu}{3} \frac{\partial E}{\partial \nu} \right] d\nu. \quad . \quad . \quad . \quad (2)$$

Thus the radiation field acts like a viscous substance (c being the velocity of light).

Brillouin proceeds to apply these ideas to the resistance of the electrons in the metal. The radiation field is replaced by the vibration field of a solid body consisting of one kind of atom, as given by Debye's theory; the moving particle is the electron. Then as

$$E(\nu) = \frac{9N}{\nu_m^3} \frac{h\nu^3}{e^{h\nu/kT} - 1}, \quad . \quad . \quad . \quad . \quad (3)$$

where N is the number of atoms per cubic centimetre and ν_m Debye's limiting frequency, equation (2) may be written

$$R = A_1 \int_0^{v_m} \alpha(v) \frac{T}{3} \frac{\partial E}{\partial T} dv, \quad . \quad . \quad . \quad . \quad (4)$$

where $4\pi/c$ before the integral is replaced by the constant A_1 . The

* L. Brillouin, *Atomes et Électrons (Rapports et discussions du Conseil Solvay, 1921, p. 192, Paris, 1923)*.

† A. Einstein and L. Hopf, *Ann. d. Physik*, **33**, 1115 (1910).

factor $\alpha(\nu)$ is originally the absorptive or scattering power of the moving particle for radiation. Now, therefore, it is a measure of the mutual action between electrons and the elastic spectrum. By replacing $\alpha(\nu)$ by a mean value $\bar{\alpha}$ outside the integral sign Brillouin obviously obtains the relationship $\rho \sim TC$.

3. The above assumption is unsatisfactory if we accept Bloch's idea that the exchange of energy between electron and elastic spectrum can only take place by quanta, i.e. that the lower the temperature the lower are the frequencies carrying the energy and hence the smaller the quantities of energy exchanged. I have therefore modified Brillouin's assumption tentatively by putting

$$\alpha(\nu) = A_2 \cdot h\nu. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As α has the dimensions of area, A_2 has the dimensions

$$[\text{Area}]/[\text{Energy}].$$

If for simplicity we put

$$\frac{h\nu}{kT} = \xi; \quad \frac{h\nu_m}{kT} = \frac{\Theta}{T} = x; \quad \frac{1}{e^{\xi} - 1} = F(\xi); \quad A_1 A_2 = A,$$

we have
$$R = \frac{1}{3} A h T \int_0^{\infty} \frac{\partial E}{\partial T} \nu d\nu,$$

and, if we bear (3) in mind,

$$R = - \frac{3}{5} A N k^2 \Theta^2 \cdot \frac{1}{x^5} \int_0^x \xi^5 F'(\xi) d\xi. \quad . \quad . \quad . \quad (6)$$

The relationship between the friction constant R and the specific resistance ρ we again take over from Brillouin. We have

$$Rv = eE, \quad nve = i,$$

where e is the charge on the electron, n the number of conducting electrons per cubic centimetre, E the intensity of the external field, and i the current density. Thus

$$\rho = \frac{E}{i} = \frac{R}{ne^2}.$$

If we substitute for R from (6) and bear in mind that

$$F'(\xi) = - \frac{1}{(e^{\xi} - 1)(1 - e^{-\xi})},$$

we obtain
$$\rho = C \frac{4}{x^5} \int_0^x \frac{\xi^4 d\xi}{(e^\xi - 1)(1 - e^{-\xi})}, \quad \dots \quad (7)$$

where
$$C = \frac{3}{4} A \frac{N}{n} \left(\frac{k}{e}\right)^2 \Theta^2. \quad \dots \quad (8)$$

Now the integral in (7) also comes into Bloch's second paper * on the resistance law at low temperatures; there, of course, it is used only in the passage to the limiting region of very low temperatures. We shall see in a moment that it also gives a satisfactory result in the region of transition from high temperatures to low.

4. Integrating (7) by parts, we obtain

$$\rho = C \left\{ \frac{20}{x^5} \int_0^x \frac{\xi^4 d\xi}{e^\xi - 1} - \frac{4}{e^x - 1} \right\}. \quad \dots \quad (9)$$

In the limiting case of high temperatures ($x \ll 1$), it follows that

$$\rho = \frac{C}{x} = C \frac{T}{\Theta},$$

i.e. we have the well-known law that ρ is proportional to the temperature, a law given by all the theories but only partially fulfilled by experiment.

In the limiting case of very low temperatures ($x \gg 1$), the second term in the brackets in (9) vanishes and in the first term we may take ∞ as the upper limit, hence obtaining †

$$\rho = 497.7 C \left(\frac{T}{\Theta}\right)^5.$$

This result is in complete agreement with Bloch's, except for the fact that Bloch's constant C has quite a different meaning.

5. For the intermediate region of medium temperatures expansions may be obtained similar to those used in the evaluation of Debye's atomic heat function.‡ To bring out this similarity we form the expression

$$\sigma = \frac{\rho}{T},$$

* F. Bloch, *Zeitschr. f. Physik*, **59**, 208 (1930); see especially p. 212.

† According to L. Brillouin, *Ann. de phys.*, **17**, 118 (1922), exact evaluation gives

$$\int_0^\infty \frac{\xi^4 d\xi}{e^\xi - 1} = 24.8862672.$$

‡ Cf. P. Debye, *Ann. d. Physik*, **39**, 789 (1912).

which for very high temperatures ($x \ll 1$) becomes

$$\sigma_x = \frac{C}{\Theta}.$$

If we introduce this relationship, (9) gives

$$\frac{\sigma}{\sigma_\infty} = \frac{20}{x^4} \int_0^x \frac{\xi^4 d\xi}{e^\xi - 1} - \frac{4x}{e^x - 1}, \quad \dots \quad (10)$$

i.e. a function of x ($= \Theta/T$), which in the high-temperature region approaches the value unity more and more closely, and in the region of very low temperatures decreases proportionally to T^4 .

To calculate the deviation from unity at a high temperature we may use the following expansion,* which only converges so long as $x < 2\pi$:

$$\frac{\sigma}{\sigma_\infty} = 1 - 4 \sum_{n=1}^{n=\infty} (-1)^{n-1} \frac{B_n}{(2n)!} \frac{2n-1}{2n+4} x^{2n}. \quad (11)$$

Here the B 's are Bernoulli's numbers

$$B_1 = \frac{1}{6}; \quad B_2 = \frac{1}{30}; \quad B_3 = \frac{1}{42}; \quad B_4 = \frac{1}{30}; \quad B_5 = \frac{5}{66}; \quad \dots$$

Thus the first few terms of the series (11) are:

$$\frac{\sigma}{\sigma_\infty} = 1 - \frac{x^2}{18} + \frac{x^4}{480} - \frac{x^6}{15120} + \frac{x^8}{518400} - \frac{x^{10}}{18627840} + \dots, \quad (11a)$$

which suffice for the calculation of σ/σ_∞ with an error of less than a tenth of one per cent for values of x less than 2.5.

For larger values of x , i.e. in the low-temperature region, we obtain † from (10)

$$\frac{\sigma}{\sigma_\infty} = \frac{497.7}{x^4} - \frac{4x}{e^x - 1} - 20x \sum_{n=1}^{n=\infty} e^{-nx} \left[\frac{1}{nx} + \frac{4}{(nx)^2} + \frac{12}{(nx)^3} + \frac{24}{(nx)^4} + \frac{24}{(nx)^5} \right]. \quad (12)$$

The first term is sufficient only for fairly large values of x . For $x = 12$ neglect of the subsequent terms would give an error of as much as 2 per cent, and the error is still 1 per cent for $x = 13$.

Some values of Θ/T , together with the corresponding values of

* See e.g. E. Madelung, *Die mathematischen Hilfsmittel des Physikers*, second edition, p. 54 (Berlin, 1925).

† The calculation is similar to that given by Debye, *loc. cit.*, p. 801.

σ/σ_∞ calculated from (11a) or (12), are given in the following table, which Dr. E. Vogt was kind enough to assist me in drawing up. For comparison Debye's values for his atomic heat function C/C_∞ are also given. At high temperatures the two functions exhibit considerable similarity; it is only at low temperatures that σ/σ_∞ decreases much more rapidly than the atomic heat. This latter behaviour, however, is exactly that exhibited by ρ/T in recent measurements with very pure metals.

TABLE I

$x = \frac{\Theta}{T}$	$\frac{1}{x} = \frac{T}{\Theta}$	$\frac{\sigma}{\sigma_\infty}$	$\frac{C}{C_\infty}$	$x = \frac{\Theta}{T}$	$\frac{1}{x} = \frac{T}{\Theta}$	$\frac{\sigma}{\sigma_\infty}$	$\frac{C}{C_\infty}$
0.25	4.000	0.9965	0.997	5.5	0.1818	0.2658	0.0758
0.50	2.000	0.9862	0.988	6.0	0.166 ₇	0.2196	
0.80	1.250	0.9653		6.5	0.153 ₈	0.1796	
1.00	1.000	0.9465	0.952	7.0	0.142 ₉	0.1471	
1.18	0.847 ₅	0.9265		8.0	0.1250	0.09910	
1.50	0.666 ₇	0.8848		9.0	0.111 ₁	0.06740	
1.69	0.591 ₇	0.8569		10	0.1000	0.04654	
2.0	0.5000	0.8074	0.825	11	0.0909 ₁	0.03270	
2.5	0.4000	0.7205	0.745	12	0.0833 ₃	0.02353	
3.0	0.333 ₃	0.6309		13	0.0769 ₂	0.01725	
3.6	0.277 ₈	0.5258		14	0.0714 ₃	0.01289	
4.0	0.2500	0.4608	0.503	16	0.0625	0.007584	
5.0	0.2000	0.3208	0.369	20	0.0500	0.003111	0.00974

6. Of the numerous observations on the resistance of metals at low temperatures, but few are suited to form a satisfactory basis for the actual functional relationships between resistance and temperature. This is partly due to the fact that the residual resistance of the metal samples is still too great for the ideal resistance to be deduced with any degree of probability, partly to the fact that sufficiently pure samples have not been investigated in the important temperature interval between $T = 4.2^\circ \text{K}$ and $T = 20.4^\circ \text{K}$. For most metals it is the values for temperatures within this very interval that would settle whether a T^5 law or a T^4 law fits the observations better.*

We shall confine ourselves to a test of formula (9) with particularly pure specimens of copper, gold, and tungsten (Tables II–IV). As usual r denotes the ratio of the resistances at temperatures T and 273.2°K . The observed values of r are used to calculate the ideal resistance by Matthiessen's rule. In the case of copper

* See also G. Borelius, *Zeitschr. f. Physik*, **54**, 806 (1929).

W. Meissner's value of only 0.0003 for the residual resistance was used, while for gold the extremely small residual resistance of 0.00029 obtained by Meissner was likewise deducted in the case of the specimen investigated by him.* Somewhat less certain, perhaps, is the reduction of the observations of Kamerlingh Onnes and Clay, for which I found the relatively large residual resistance 0.00223 in Kamerlingh Onnes and Tuyn's table.† For the tungsten crystal the residual resistance was measured by Meissner.

TABLE II
Copper: $\Theta = 330$

T	$r_{\text{cal.}}$	$\frac{r_{\text{obs.}} - 0.0003}{1 - 0.0003}$
273.2	1	1
195.2	0.662	0.658
90.2	0.1847	0.1804
81.2	0.1451	0.141
20.4	0.00059	0.0005 ₁
4.2	0.00000	0.0000 ₀

TABLE III
Gold: $\Theta = 175$

T	$r_{\text{cal.}}$	$\frac{r - 0.00029}{1 - 0.00029}$ (Meissner).	$\frac{r - 0.00223}{1 - 0.00223}$ (K. Onnes and Clay)
273.2	1	1	1
87.43	0.264 ₃	0.2551	
78.86	0.227 ₆	0.2187	
57.8	0.1356		0.1314
20.4	0.00604	0.0057 ₂	0.0059
18.0	0.00346		0.0035
14.3	0.00117		0.00137
12.1	0.00051		0.00048
11.1	0.00033		0.00030
4.2	0.000002 ₆	0.00000 ₃	

* The single-crystal bar Au 11 was selected (W. Meissner, *Zeitschr. f. Physik*, **38**, 647 (1926)).

† *Leiden Commun., Suppl.*, **58**, 17, 18 (fig. 3). I had previously (*Handbuch der Physik*, **13**, p. 21) estimated the residual resistance of this specimen at 0.00210.

TABLE IV
Tungsten: $\Theta = 346$

T	$r_{\text{cal.}}$	$\frac{r_{\text{obs.}} - 0.00058}{1 - 0.00058}$
273.2	1	1
90.2	0.176	0.168
87.4	0.163	0.156
77.6	0.122	0.115
20.4	0.00049	0.0005 ₀

I would specially like to emphasize the very satisfactory agreement with observation in the case of copper, where the empirical formula ($\rho \sim TC$) fails. But even in the case of gold the new formula seems preferable, especially as we can then use a value of Θ (175) which is closer to the value calculated from C_v by Clusius and Harteck* than that which was previously used (190). Why so great a difference should arise for $T = 14.3^\circ$ I cannot say. In all three metals the observed and calculated temperature coefficients, i.e. the differences between successive values of r , agree remarkably well. On the other hand, I have usually adjusted matters so that $r_{\text{cal.}}$ comes out a few per cent greater than the reduced $r_{\text{obs.}}$. This is connected with the fact that while theory requires direct proportionality to T as the limiting law for high temperatures, experiment nearly always gives a more rapid rise, i.e. a smaller value of r at low temperatures. Just as this increase was taken account of in the statement of the empirical law by the introduction of C_p instead of C_v , we could also (according to Debye) imagine $(\partial E / \partial T)_v$ in equation (4) (p. 47) replaced by an expression corresponding to the change of energy density at constant pressure.

In many cases this procedure would suffice, but not in all. At high temperatures the resistance-temperature curve no longer has any universal character.† For example, the metals platinum, palladium, and tantalum at high temperatures exhibit a retarded rise in the resistance, which is very striking but so far is completely unexplained, while the ferromagnetic metals iron, nickel, and cobalt

* K. Clusius and P. Harteck, *Zeitschr. f. phys. Chemie*, **134**, 243 (1928): Θ varies between 186 and 163.

† Thus Frenkel and Mirolubow's expression (*Zeitschr. f. Physik*, **49**, 892 (1928)) for the fall in conductivity at high temperatures as a power series in Θ/T does not correspond to the facts.

exhibit a very markedly accelerated rise in resistance up to the Curie point. For this Gerlach * gives the plausible explanation that the spontaneous magnetization which occurs below the Curie point, i.e. the magnetic orientation of the electrons within the magnetic elements, leads to a fall in the resistance.

We have still to explain why lead and platinum are not also used to test the formula. For these are the very metals used in resistance thermometry, so that numerous observations of their behaviour at low temperatures are available, and it is for these metals that the empirical formula $\rho \sim TC$ works particularly well.† Here, therefore, the new formula might be expected to fail. In this connexion we must bear in mind the fact that though lead has been investigated in a very pure state it is very questionable from the experiments with Cu, Au, &c., whether the existence of a residual resistance in r amounting to a few units multiplied by 10^{-4} should not be assumed. Direct measurement of it is impossible, as it vanishes at the point where the resistance suddenly changes. It might, however, be possible to extrapolate to it by using a magnetic field to destroy the superconducting state. At any rate lead meanwhile gives data in favour of the T^4 or T^5 law. In the case of platinum a comparatively large residual resistance has to be put up with, especially in the specimens which were investigated in detail at Leiden. This gives rise to an uncertainty in the extrapolation to the ideal resistance which has led me to leave platinum out of account meanwhile.

7. Although, as we have said above, the main features of the relationship between the electrical resistance and the temperature are duly reproduced by formula (9), p. 49, except in the case of high temperatures, this does not mean that we have explained the problem theoretically at all. For the method of deducing the formula which I gave above has no secure theoretical basis. Bloch has also informed me that he is unable to establish formula (9) for the intermediate region above the region where the T^5 law holds. Peierls, on the contrary, is convinced that his extension to Bloch's theory, which leads to a T^4 law, is justified. Houston, on the other hand, obtained in his second paper ‡ a resistance law which is similar to Bloch's but far from identical with it. The results of his experiments with gold are less favourable than those given in Table III.

In another direction, moreover, the new theories fail to meet

* W. Gerlach, *Zeitschr. f. Physik*, **59**, 847 (1930).

† *Handbuch der Physik*, **13**, 20, 21. The values of Θ used there, however, are certainly high enough.

‡ *Phys. Rev.*, **34**, 279 (1928).

sundry requirements of the experimental physicist. Most of them give the absolute value of the electrical resistance. It turns out, however, that the expressions obtained differ greatly among themselves, although they do give the right order of magnitude. Hitherto none of the theories has given a satisfactory explanation of the order of metals as regards conductivity, e.g. why silver and copper are the best conductors and conduct about equally well.* Attempts to calculate the anisotropy of the resistance in non-regular crystals have hitherto met with just as little success, although Houston's attempt in his first paper to explain it by different binding forces between the atoms in different directions leads to a result of the right order for cadmium (though, to be sure, for high temperatures only).†

In addition, it is not clear how the characteristic temperature Θ enters into ρ . While Houston obtains $\rho \sim \Theta^{-1} f_1(\Theta/T)$ in his first paper (*Zeitschr. f. Physik*, **48**, 449 (1928)) and $\rho \sim f_2(\Theta/T)$ in his second paper (*Phys. Rev.*, **34**, 279 (1928)), Bloch and Peierls obtain $\rho \sim \Theta^{-2} f_3(\Theta/T)$. But the way in which Θ is involved determines the effect of pressure on the electrical resistance.‡

* See e.g. Table II in Houston's first paper (*Zeitschr. f. Physik*, **48**, 449 (1928)), where the alkali metals agree very badly with the theory.

† An approximate calculation of the fall of resistance with temperature in Zn and Cd (\parallel and \perp), likewise based on the elastic anisotropy, has been made by Grüneisen and Goens, *Zeitschr. f. Physik*, **26**, 250 (1924).

‡ If we put $\rho = P\Theta^{-z} f(\Theta/T)$, where P comprises all the factors which depend on the pressure except Θ and the temperature function, which, as we know, is a function of Θ/T at low temperatures, we have

$$\frac{1}{\rho} \left(\frac{d\rho}{dp} \right)_T = \frac{1}{P} \frac{\partial P}{\partial p} - \frac{z}{\Theta} \left(\frac{\partial \Theta}{\partial p} \right)_T - \frac{T}{f} \left(\frac{\partial f}{\partial T} \right)_p \frac{1}{\Theta} \left(\frac{\partial \Theta}{\partial p} \right)_T.$$

Now as $\frac{1}{f} \left(\frac{\partial f}{\partial T} \right)_p$ is practically identical with $\frac{1}{P} \left(\frac{\partial P}{\partial p} \right)_T$, i.e. with α_T , the temperature coefficient of electrical resistance, referred to the temperature T under consideration, we may write

$$\frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T = \frac{1}{P} \frac{\partial P}{\partial p} - \frac{1}{\Theta} \left(\frac{\partial \Theta}{\partial p} \right)_T [z + \alpha_T T].$$

This shows what an important part is played by the exponent z . For at the freezing point $\alpha_T T$ is about equal to unity, and e.g. for $z = 1$, $\frac{1}{P} \left(\frac{\partial P}{\partial p} \right)_T$ would often make only a small contribution to the total effect. In the calculation of $\frac{1}{\Theta} \left(\frac{\partial \Theta}{\partial p} \right)_T$ we may make use either of the Madelung-Einstein relationship between Θ and the compressibility (Houston, *Phys. Rev.* **34**, 283 (1928)), or of the equation

$$\frac{1}{\Theta} \left(\frac{\partial \Theta}{\partial p} \right)_T = \frac{1}{C_v} \left(\frac{\partial V}{\partial T} \right)_p$$

(E. Grüneisen, *Handbuch der Physik*, **10**, 35, equation (48); **13**, 70, equation (27)).

I should like to draw attention to a remarkable coincidence—I cannot regard it as anything else—in the argument given above in section 3 (p. 48). The constant C in equation (8) gives the correct order of magnitude for the specific resistance in electrostatic units if we put $A = 4\pi/3 \cdot 10^{10}$, i.e. if we leave $A_1 = 4\pi/c$ in equation (4) and make A_2 of the order of unity. As the velocity of light can hardly enter into the expression for the electrical resistance and, as we mentioned above, A_2 is not a pure number but has the dimensions [Area]/[Energy], this result can scarcely be regarded as significant. Even the occurrence of Θ^2 as a factor in C (equation (8)) can only be made to agree with the decrease of the resistance with rise of pressure if A contains quantities depending on the pressure.

8. The most interesting aspect of conduction by electrons, namely superconduction, in which experiment is continually providing us with fresh surprises, scarcely falls within the scope of this lecture, as so far there exists no theory of superconduction to test. Such a theory would have to explain the characteristic conditions under which superconduction occurs, the change in the order of magnitude of the resistance, and the temperature at which the change of resistance takes place. Even empirical relationships for these have still to be discovered.

One further remark. Whereas it has usually been assumed hitherto that an essential change in the mechanism of conduction takes place at the point where the resistance changes, Kapitza has recently put forward the idea that the resistance in the superconducting state is the ideal resistance for the metal at the temperature in question and that above the point where the resistance changes it is merely cloaked by additional resistances which vanish at the point of transition.

I cannot agree to this idea any more than Meissner and Scheffers* do. If anything is certain, it is the fact that the rates of decrease of resistance in different metals at temperatures proportional to their Θ 's are comparable. The temperature of transition for lead corresponds to a temperature of 26° for copper, i.e. to a temperature for which, as we saw above, the fall of resistance is in complete agreement with formula (9), which at this point yields a resistance approximately proportional to T^5 . In Cu, at any rate, the resistance falls off in such a way that the validity of the formula is maintained until the temperature 4.2° K is reached. If we apply the formula to lead at the temperature of transition, we obtain a

* W. Meissner and H. Scheffers, *Phys. Zeitschr.* 20, 827 (1929).

resistance of the same order of magnitude as that observed at higher temperatures, and not one smaller by several powers of ten.

The Temperature Law of Thermal Resistance

9. Peierls * has recently put forward a theory of the thermal conductivity of metals and its relationship to the electrical conductivity which leads to the following important results:

(a) The flow of energy transported by the lattice vibrations is small compared with the total flow of energy, especially at low temperatures. We certainly must not regard the process as if the conductivity were an additive combination of conduction by the lattice alone and conduction by the electrons alone, for these are not independent of each other. According to Peierls, the electrons play a preponderant part in the restoration of the thermal equilibrium of the lattice vibrations once it has been disturbed. Additivity of the thermal resistances must also be rejected.

(b) At high temperatures the thermal resistance w is constant, while in the limiting region of low temperatures it decreases proportionally to T^2 . Peierls' theory has nothing to say about the intermediate region.

(c) As Peierls obtains a T^4 law for the electrical resistance in the limiting case, he concludes that the ratio of the electrical and thermal resistances does not decrease proportionally to T , but to T^2 , or in other words: at low temperatures the Wiedemann-Franz-Lorenz quantity ρ/Tw should not be constant, but should decrease proportionally to T .

Peierls' first result is very remarkable, for according to Eucken crystals of insulators exhibit a thermal conductivity which increases rapidly with fall of temperature and is far from trifling compared with that of metals. Eucken † therefore believes that a very considerable portion of the total heat flow may be ascribed to the lattice vibrations. For experimental reasons which I will go into later, I cannot reconcile myself to Eucken's ideas, ‡ and therefore I look to Peierls' conclusion, that the lattice vibrations have no appreciable effect and that simple addition of the conductivities is quite out of the question, for the possibility of a satisfactory solution.

* R. Peierls, *Ann. d. Physik*, **4**, 121; **5**, 244 (1930).

† A. Eucken, *Leipziger Vorträge*, 1928 (S. Hirzel, Leipzig, edited by H. Falkenhagen), p. 112; *Zeitschr. f. phys. Chemie*, **134**, 220 (1928).

‡ Cf. E. Grüneisen, *Zeitschr. f. phys. Chemie*, **1**, 379 (1928); *Zeitschr. f. Physik*, **51**, 652 (1928).

Whether Peierls' other statements ((b) and (c)) are true or not cannot be definitely settled at present, as they refer only to the limiting regions of low and high temperatures and say nothing about the intermediate region.

Obviously very many observations on very pure metals at very low temperatures will be required if we are to decide on such grounds alone whether the thermal resistance follows a T^2 law or a T^3 law. Sufficient observations are not available at present.

10. Nevertheless, observation suggests that in the intermediate region the thermal resistance falls off more rapidly than T^2 . Let us compare (as at first glance seems simple enough), e.g. the thermal resistances at 21.2°K and 83.2°K for several metals with large values of Θ , such as Cu, W, Rh, Al. If $[w] \sim T^2$ were valid up to such a high temperature, the ratio of the resistances would have to be $(83.2/21.2)^2 = 15.4$. We should expect to get lower values than this. Instead we obtain, in the case of the metals mentioned:

	Cu	W	Rh	Al
$\frac{[w]_{83.2}}{[w]_{21.2}} =$	20	19	36	20.

Thus the thermal resistance falls away more rapidly than T^2 between 83.2°K and 21.2°K .

Here, to be sure, we must note that these numbers are not directly observed, but extrapolated to the case of the ideally pure metal by means of the equation *

$$w = [w] + \frac{\zeta}{ZT}, \quad \text{i.e. } [w] = w - \frac{\zeta}{ZT}, \quad . \quad . \quad (13)$$

where $[w]$ is the thermal resistance of the ideally pure metal, ζ the residual electrical resistance, which at the lowest temperatures is invariable, and Z is a constant which in general may be taken equal to the Wiedemann-Franz-Lorenz constant $2.2 \cdot 10^{-8}$ [watt-ohm/deg.²] W. Meissner has measured the residual resistance ζ for the very pure specimens of the above-mentioned metals investigated by Goens and myself,† so that we are in a position to find $[w]$ by applying a correction to w . The correction is trifling for 83.2°K , but considerable for 21.2°K . For this temperature, therefore, we shall give the detailed data.

* Ger. Gleichung der isothermen Geraden.

† E. Grüneisen and E. Goens, *Zeitschr. f. Physik*, **44**, 615 (1927).

TABLE V

Calculation of the Thermal Resistance of Ideally Pure Unhardened Metals at 21.2° K in [cm. deg./watts]

	Cu.	W.	Rh.	Al.
$10^6 \cdot \zeta$	0.00089	0.00285	0.0137	0.0168
$10^8 \cdot ZT^*$	35.8	46.7	46.7	46.7
ζ/ZT	0.0024	0.0061	0.0294	0.0360
$w_{\text{obs.}}$	0.0114	0.0292	0.0420	0.0500
$[w]_{21.2^\circ}$	0.0090	0.0231	0.0126	0.0140

The values of $[w]$ for Rh and Al are very uncertain, as here the values of ζ are no longer very small. We may, however, say with great probability that the values of $[w]$ represent upper limits (cf. section 13, p. 61). Thus the values given above for the ratios are more likely to be too low than too high. So much the more do they contradict the validity of the T^2 law in the range of temperature considered.

11. Nevertheless, such a law might be valid in the limiting region. The empirical function,

$$[w] = [w]_{\infty} \left(1 + k \frac{\Theta}{T} \right) \frac{C}{C_{\infty}} \quad . \quad . \quad . \quad (14)$$

(C being the atomic heat function), put forward by Goens and myself, also has the property of gradually passing into a T^2 law after a more rapid fall to begin with. Thus, as long as our empirical formula holds Peierls' result might also be right.

Now it has been proved that this formula in combination with equation (13) does reproduce the main features of the variation of the thermal resistance with temperature for arbitrary specimens of a metal.† But systematic deviations were immediately observed to occur, the Debye function $C(\Theta/T)$ falling off *too slowly* at very low temperatures with the value of Θ obtained from the atomic heat. Thus the empirical formula cannot well be taken as a proof of Peierls' T^2 law.

* See section 13 (p. 61) for the choice of Z in the case of Cu.

† Cf. the tables and graphs in *Zeitschr. f. Physik*, **46**, 151 (1927), or in *Atti del Congresso Intern. dei Fisici*, Como, **2**, 105 (1928).

TABLE VI

$[w]$, the Specific Thermal Resistance of Copper, reduced to the Pure, Annealed State

T	$[w]$ obs. and red.	$[w]_{\text{cal.}}$ according to (14a).		$[w]_{\text{cal.}}$ according to (14)
		$\Theta = 330$ $k = 1/5.5$ $[w]_{\infty} = 0.226$	320 $1/6$ 0.228	335 $1/8$ 0.2394
373.2	0.255	0.251	0.250	0.255
273.2	0.255	0.255	0.253	0.255
83.2	0.179	0.181	0.181	0.179
21.2	0.0090	0.0073	0.0077	0.0140

12. As even in the empirical formula for the electrical resistance ($\rho \sim TC$) the C function falls away too slowly and may with advantage be replaced by the function σ (equation 10), giving Bloch's T^5 law, it is natural to attempt to make a similar change in formula (14) for the thermal resistance, i.e. to put

$$[w] = [w]_{\infty} \left(1 + k \frac{\Theta}{T}\right) \frac{\sigma}{\sigma_{\infty}} \quad . \quad . \quad . \quad (14a)$$

In the limiting case of very low temperatures this gives $[w]$ proportional to T^3 , in contradistinction to Peierls' theory; on the other hand, the Wiedemann-Franz-Lorenz quantity $[\rho]/T[w]$ would again come out proportional to T , as required by Peierls. In Table VI the formulæ (14) and (14a) are compared with the results of experiment in the case of copper. At very low temperatures formula (14a) agrees better than (14), and at high temperatures not much worse, especially if Θ is taken equal to 320, a value which agrees with the observations of the atomic heat but, of course, is unfavourable for Table II. In spite of the amply high value of Θ , formula (14) gives too gradual a decrease towards 21.2° K.

This result points to a limiting T^3 law rather than to a T^2 law, but of course the empirical formula does not prove much so long as it is not supported by more points of observation. The comparatively large decrease in $[w]$ as the temperature becomes high ($[w]_{\infty} = 0.226$ or 0.228) is not confirmed by experiment.

The Wiedemann-Franz-Lorenz Law and the Linear Law connecting Thermal Resistance, Electrical Resistance, and Temperature

13. In section 10 (p. 58) we used equation (13),

$$w - [w] = \frac{\zeta}{ZT} \quad \text{or} \quad \Delta w = \frac{1}{Z} \frac{\Delta \rho}{T},$$

to extrapolate for the thermal resistance to the ideally pure metal. We may therefore appropriately say a few words about the experimental and theoretical basis for this equation.

Experimentally it was found that at constant temperature the increase in the thermal resistance caused by deformation or formation of mixed crystals (*static* disturbances of the lattice) is to a remarkable degree of accuracy proportional to the increase of the electrical resistance divided by the absolute temperature.* If we compare the above formula with the Wiedemann-Franz-Lorenz law for pure metals,

$$[w] = \frac{1}{[L]} \frac{[\rho]}{T},$$

which expresses the relationship between the thermal resistance caused by *thermal* disturbance and the corresponding electrical resistance, we obtain the following result: $[L]$ at high temperatures and Z at low temperatures have the approximate value $2.2 \cdot 10^{-8}$, which is also in approximate agreement with the classical theoretical value. $[L]$ falls with decreasing temperature (for Cu to one-third of its value between 291°K and 21.2°K), whereas Z increases somewhat as the temperature rises, in some metals (W, Fe) to a not inconsiderable extent. Thus for any temperature

$$Z > [L].$$

In the very case of copper, however, Goens and I found that for very small disturbances of the lattice the value $Z = 2.2 \cdot 10^{-8}$ is not reached; for example, reliable measurements of our purest specimens of copper † at 21.2°K gave the following results:

	$\rho/T \cdot 10^9$	w
Cu 2b	0.0882	0.0114
Cu 4a	0.1915	0.0175

$$\frac{\Delta \rho}{T} = 0.1033 \quad \Delta w = 0.0061 \quad Z = \frac{\Delta \rho}{T \Delta w} = 1.69 \cdot 10^{-8}.$$

* Cf. Grüneisen and Goens, *Zeitschr. f. Physik*, **44**, 615 (1927); and, in particular, the tables in *Zeitschr. f. phys. Chemie*, B, **1**, 379 (1928).

† Grüneisen and Goens, *Zeitschr. f. Physik*, **44**, 615 (1927), Table V, Cu 2b and Cu 4a.

In the graphical representation of the linear law (equation 13, p. 58) this failure to reach the normal value of Z for larger disturbances of the lattice is shown by the fact that the Cu isothermal at 21.2°K bends downwards at the end nearest the absolute zero. We did not obtain this result with gold or with aluminium. In order that it should occur at 21.2°K , it seems necessary that extreme purity and a high value of Θ should co-exist, as in Cu 2b. The gold certainly was very pure, but gold has a small value of Θ , and aluminium, though it has a large value of Θ , cannot be obtained nearly so pure as Au and Cu.

At any rate it follows that in the extrapolation for the thermal resistance to the ideally pure metal (Table V) we must take Z as being at most equal to $1.69 \cdot 10^{-8}$ in the calculation of $[w]$ for Cu 2b, and that in the other metals, where the existence of a downward bend cannot be proved and Z is accordingly put equal to $2.2 \cdot 10^{-8}$, we may possibly obtain too small a value for Δw , i.e. too large a value for $[w]$.

Now as regards the statements made by theory, Peierls requires that $[L]$ should decrease towards the absolute zero, as we explained above (section 9, p. 57). But Peierls also holds that the constancy of Z at low temperature is "intelligible, if the additivity of the 'ideal' resistance and the 'residual resistance' . . . is strictly valid, both for electrical conductivity and thermal conductivity". For the classical theorem on the number of collisions is justified even at *low* temperatures for the statical lattice disturbances regarded as causing the resistance, whereas it is not so for the thermal agitation here.

This being so, we could conclude, from the fact that Z at low temperatures approaches the classical numerical value, that here the effect of the lattice vibrations on the thermal conductivity really recedes into the background, as Peierls' theory also requires. On the other hand, the fact that at higher temperatures Z has larger values would have to be interpreted to mean that owing to the effect of the lattice vibrations the thermal resistance is raised by statical disturbances of the lattice to a smaller extent than would occur if the lattice vibrations had no effect. In order to understand the experimental details, it would be necessary—here I agree wholeheartedly with Eucken—to analyse accurately the part played by the lattice vibrations in the total flow of heat. According to Peierls' theory, however, this would seem to be far from easy, as the conduction due to the electrons and the conduction due to the lattice cannot be combined by simple addition.

The Mutual Action of Electrons in Metals

F. BLOCH, HAARLEM

In the electron theory of metals no accurate allowance has hitherto been made for the effects of the conduction electrons on each other. Drude and Lorentz even went the length of assuming that to a first approximation the mutual action of the electrons and ions may be neglected, and accordingly spoke of a gas of "free" electrons.

From the point of view of classical mechanics this free mobility of the electrons, which experiment clearly requires as a distinguishing feature of metals, perforce remained mysterious; the actual order of magnitude of the forces exerted on an electron by the other electrons and the atomic residues would give the electron a mean free path equal to a small multiple of the distance between the atoms, whereas Sommerfeld has shown that if we use the Fermi statistics the observed values of the conductivities of metals are not obtained unless we assume that the mean free path amounts to several hundred times the interatomic distance.



Fig. 1

According to the quantum mechanics it was possible to show in the first place that even when the effect of the ions is very marked an electron does move freely through the lattice, provided we assume that the presence of the remaining electrons is merely manifested in a screening effect due to their being concentrated about the atoms. For then, owing to the lattice structure, the electron is situated in a periodic potential field with strong maxima at the ions (fig. 1), and owing to its undulatory nature its freedom to move arises in the same way as in the familiar case of the rectilinear propagation of a light wave in a medium with a periodic refractive index. This is shown by the form of the proper functions,

$$\psi_k = e^{i(kr)} u_k(r),$$

which only differ from the plane waves of motion in the absence of

external forces by a modulating factor $u_k(r)$ with a period equal to the interatomic distance.

On the other hand, it still remained a mystery how it is that the mutual action of the electrons does not completely destroy the free mobility of the electron. For this mutual action is not, as might be expected, a feeble one, but is of the same order as that between the atoms and the electrons, and certainly cannot be completely explained by a screening effect. If in the total potential acting on an electron,

$$V = V_{\text{ions}} + \sum V_{\text{other electrons}},$$

we begin by regarding the part remaining after the screening effect has been deducted as a small perturbation, it gives rise to transition processes which may be interpreted as collisions and exchanges of electrons. A simple estimate shows that even at normal temperatures these processes are about ten times as numerous as those arising from the lattice vibrations and that their effect is still more marked at lower temperatures; Peierls has also shown that collisions have an important effect on the electrical resistance. Besides, the exchange energy of the electrons is of the same order of magnitude as the energy of the mutual action of electrons and lattice.

It follows from the above that the mutual action of the electrons may *not* be regarded as a feeble disturbance, and we have therefore attempted to see whether the characteristic features of metals cannot be recovered from the other limiting case where the mutual action is on the contrary assumed to be very strong.

Remembering that a metallic crystal is nothing but a very large molecule, we shall use the same methods of approximation for the investigation of the motion of the electrons as have hitherto been employed in the theory of molecular structure. We shall have to be prepared for the same difficulties about the convergence of the approximation process, which arise from the fact that the mutual action of the electrons and ions is of the same order of magnitude as that between the electrons themselves; on the other hand, however, the particularly simple periodic structure of the crystal causes the method to be more effective than for polyatomic molecules, which are generally complicated.

If we confine ourselves in the first instance to the case of *one* conduction electron per atom, the two main methods of approximation under consideration (in which it is assumed that the mutual action of the electrons is weak, or strong) as applied to molecular

structure may be illustrated very simply by means of a diatomic molecule, e.g. H_2 (fig. 2).

In the first case, we should in the first instance have to investigate each of the electrons 1 and 2 in the field of the two force-centres a and b . The proper functions are then symmetrical or anti-symmetrical with respect to the medial plane M , i.e. in passing from a to b they are multiplied by ± 1 , whereas we saw above that in the case of several equal equidistant hollows the proper functions are multiplied by an arbitrary root of unity in passing from one atom to the next. If we assume that the hollows are very deep or very far apart, the proper functions may be represented approximately in terms of ϕ_a , ϕ_b , the proper functions of the individual atoms, as follows:

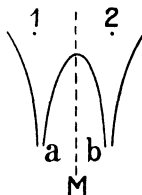


Fig. 2

$$\psi_{\pm} = \phi_a \pm \phi_b, \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

or in a linear chain of N atoms

$$\psi_{\xi} = \sum_f e^{if\xi} \phi_f, \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

where

$$\xi = 2\pi \frac{\text{integer}}{N}$$

and ϕ_f is the proper function of the f^{th} atom.

We see at once that it is quite inadmissible to assume here that the mutual action of the electrons is feeble; for it might happen that the two electrons belonged to the *same* atom, so that a strong repulsion would result.

The second method, that of Heitler and London, takes account of this by starting from the assumption that, at least for the molecular state in which the energy is least, both electrons are never to belong to the same atom. If in addition we take account of the exclusion principle (here the *spin* must be considered), the method may be simply described as an attempt to represent the actual proper functions of the problem approximately by the following functions, which are antisymmetric in the electrons:

$$\begin{aligned} \psi_{ab} &= \begin{vmatrix} \phi_a^r(x_1) & \phi_a^r(x_2) \\ \phi_b^r(x_1) & \phi_b^r(x_2) \end{vmatrix}; & \psi_a &= \begin{vmatrix} \phi_a^r(x_1) & \phi_a^r(x_2) \\ \phi_b^l(x_1) & \phi_b^l(x_2) \end{vmatrix}; \\ \psi_b &= \begin{vmatrix} \phi_a^l(x_1) & \phi_a^l(x_2) \\ \phi_b^r(x_1) & \phi_b^r(x_2) \end{vmatrix}; & \psi &= \begin{vmatrix} \phi_a^l(x_1) & \phi_a^l(x_2) \\ \phi_b^l(x_1) & \phi_b^l(x_2) \end{vmatrix}. \end{aligned}$$

The lower index of ψ indicates on which atom the spin is in a prescribed direction, e.g. to the right (indicated by the upper index r of the function ϕ).

Now, provided we neglect magnetic energy, the perturbation calculation gives the result that to a zero order approximation we have to take

$$\psi_{ab}, \psi, \text{ and also } \psi_{\pm} \text{ (equal to } \psi_a \pm \psi_b). \quad . \quad . \quad (2a)$$

The energy of perturbation of the first three solutions to a first approximation is

$$\epsilon = 0$$

(except for an additive constant), and that of the fourth is

$$\epsilon = -2\mathcal{J} = -2 \int \phi_a(x_1) \phi_b(x_2) \left[\frac{2e^2}{r_{12}} + V(x_1) + V_b(x_1) + V(x_2) + V_b(x_2) \right] \phi_a(x_2) \phi_b(x_1) dx_1 dx_2,$$

where \mathcal{J} is the well-known Heitler-London exchange integral.

The Heitler-London method, which is obviously a suitable method of approximation when we assume *strong* repulsion of the electrons, was first applied to the crystal by Heisenberg in his theory of ferro-magnetism.

To obtain more accurate information about the proper functions, we may (again approximately) assume them expressed as linear aggregates of the functions $\psi, \psi_f, \psi_{fg},$ &c., which are anti-symmetric in the electrons, i.e. of determinants in which the lower index indicates in which atom the spin is towards the right. Provided we neglect magnetic forces, we again need only combine those functions which have the same spin moment, i.e. an equal number of indices.

A very simple case is that of a single spin towards the right. Here the correct linear-aggregate extension of (2a) is

$$\psi_{\xi} = \sum_f e^{i f \xi} \psi_f, \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

and the corresponding energy is

$$\epsilon_{\xi} = -\mathcal{J}(1 - \cos \xi).$$

We have written (2a) and (2b) in the same form as (1a) and (1b) in order to bring out the formal analogy between the position of the spin directed towards the right in the crystal and that in the single electron investigated previously. This may also be expressed by

saying that here it is no longer the single electron but the single spin that moves "freely" through the crystal, so that we may speak of "spin waves" instead of "electron waves".

Broadly speaking, the same is also true when there are several spins directed towards the right, even when the numbers of the spins to right and to left are of the same order of magnitude. We have then merely to describe the state of the metal not by *one* number ξ , but by as many numbers ξ_j as there are spins directed towards the right, and the energy is approximately given by

$$\epsilon = -J \sum_j (1 - \cos \xi_j).$$

Owing to the fact that the spins directed towards the right cannot be distinguished among themselves, we may not regard states ob-

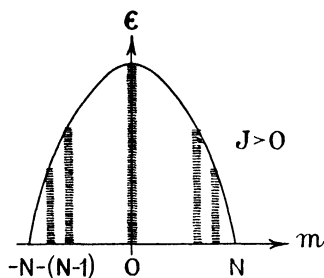


Fig. 3a

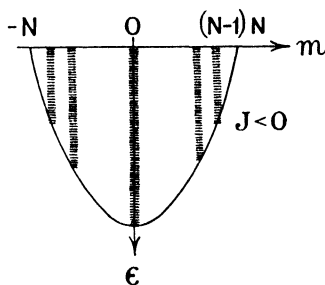


Fig. 3b

tained merely by exchanging the ξ_j 's as different; this means that we have to apply the Bose-Einstein statistics to the spins. But the analogy with a Bose-Einstein gas is purely formal. For the electrons, of course, we have the exclusion principle, which has already been taken account of in the antisymmetric forms assumed for the proper functions.

That we can still deal with the case where there are a large number of spins directed towards the right depends on the fact that then we need consider only a mean spin density and may disregard its variations; if we also neglect the small changes of energy caused by these variations, we obtain the whole spectrum of the metal to a first approximation. It is roughly of the form shown diagrammatically in fig. 3, in which the energy values associated with each value of the resultant magnetic spin moment in a definite direction (expressed in terms of Bohr magnetons) are plotted as ordinates.

If, as we must assume, the moments of momentum associated

with the motion of the electrons in the metal in general cancel each other, the essential features of the magnetic properties of the metal are determined by the electronic spin.

Fig. 3*a* represents the case of ferromagnetism which was investigated by Heisenberg and which occurs when $\mathcal{J} > 0$. For this it is essential that at sufficiently low temperatures the states with different magnetic moments should all be equally probable, so that strong magnetization may arise even in a very feeble external field.

In fig. 3*b* we have the commoner case of a feebly paramagnetic metal. For $kT \ll -\mathcal{J}$ the probability that a definite magnetic moment M should occur is given essentially* by

$$e^{-\frac{1}{kT}(\frac{c}{2} \frac{M^2}{N} - HM)}, \quad c \sim \frac{\mathcal{J}}{\mu^2},$$

where μ is Bohr's magneton, and its maximum is given by

$$\frac{M}{N} = \frac{H}{c} \sim \frac{H\mu^2}{\mathcal{J}}.$$

That is, the susceptibility

$$\chi = N \frac{\mu^2}{\mathcal{J}}$$

is independent of the temperature and is of the observed order of magnitude for $\mathcal{J} \sim 1$ volt. Thus we see that the deviation from the classical Curie law which arises from the exclusion principle, a deviation which was previously evaluated by Pauli for the case of free electrons, holds good even when the mutual action is strong.

The important fact that the quantum theory explains the extraordinarily small specific heat of electrons at normal temperatures, as is well known, was pointed out by Sommerfeld. Our model likewise explains this fact, though in a somewhat different way. If, as is permissible here, we work with the spins in the same way as we previously did with the free electrons, it follows by what we have said above that we have to deal with a degenerate Bose-Einstein gas, the specific heat of which at low temperatures is, as we know, given by

$$C_v = R \left(\frac{T}{T_0} \right)^{\frac{3}{2}}.$$

The temperature of degeneration, $T_0 \sim \mathcal{J}/k$, of course lies far

* [In this paper the sign \sim means "approximately equal to".]

above normal temperatures, so that here again the electrons contribute very little to the specific heat. It would be interesting if we could find out experimentally whether the mutual action of the electrons really makes its influence felt here, as if it did not exist we should according to Sommerfeld expect the specific heat to be a linear function of the temperature.

In order to prove that the method described here really reproduces metallic properties correctly, it is essential that in this case also, lattice vibrations being neglected, we should have stationary states of the metal in which a current flows through it, i.e. "free" mobility of the electrons.

Again it is sufficient to point to the analogy between the "spin" occurring here and the motion of a single electron investigated previously. In fact, the proper function (2*b*), e.g. in the case of a spin directed towards the right gives a mean current proportional to $\sin \xi$ and of the same order of magnitude, just as (2*a*) was shown to do above for an electron. Here, of course, the current is the result of a complicated joint motion of the individual electrons, as may naturally be expected even when their mutual action is carefully borne in mind.

Finally, we may again take account of the lattice vibrations also and thus be enabled to calculate the electrical resistance. We must then remember that the exchange integral is no longer the same for all pairs of neighbouring atoms, but varies from place to place and from time to time with the vibrations of the atoms. If we carry out the formal calculation with the spin waves as we previously did with the electron waves, we again obtain a definite finite current under the action of an external electric field. Though this readily leads to a value of the right order of magnitude for the resistance, a more exact determination of its magnitude and temperature variation would seem to require further extensive calculations.

The Behaviour of Metallic Conductors in Strong Magnetic Fields

R. PEIERLS, ZÜRICH

The fact that the resistance of a metal alters when it is subjected to the action of a magnetic field has been known for a long time, and a qualitative explanation was available even on the classical electron theory. As a result of the magnetic field, of course, the paths of the electrons in the metal are no longer straight, but curved, so that an electron moving through the metal has to traverse a longer distance in order to pass from one side to the other, and thus has a greater chance of colliding with atoms of the lattice on the way.

This simple way of looking at the matter immediately leads to the result that no change of resistance should arise if the magnetic field is parallel to the direction of the current, for the component of motion parallel to the magnetic field is not modified by the field. On the contrary, however, experiments show that though the change of resistance in this case is noticeably smaller than in the case of a transverse field, it still remains of the same order of magnitude.

A quantitative discussion of the effect was not possible until a more accurate idea of the phenomena occurring in metallic conduction had been obtained from the application of the Fermi statistics to the electrons.* In Sommerfeld's calculations of the change of resistance it turned out that, as might be expected, the theory did lead to a result of this kind. In these calculations the effect of the magnetic field on the motion of the electrons was regarded as a small perturbation, i.e. the resistance was expanded in powers of the intensity of the magnetic field. In this expansion, of course, only even powers can occur, since the resistance must be independent of the sign of the magnetic field, and a change in the resistance which is proportional to the square of the intensity of the magnetic field is thus obtained.

On Sommerfeld's theory, however, the coefficients turn out to

* A. Sommerfeld, *Zeitschr. f. Physik*, **47**, 1 (1928).

be of an order of magnitude smaller by several powers of ten than that given by experiment.

As might be expected, Sommerfeld's theory also makes the longitudinal effect vanish. Thus there are two contradictions between theory and experiment. A third difficulty arose when Kapitza * and Meissner and Scheffers † made experiments with strong magnetic fields at low temperatures and showed that even at intensities which are quite easily attained the effect ceases to be proportional to the square of the intensity. In the strongest fields hitherto obtained the change of resistance is a linear function of the intensity.

In order to solve this difficulty Bloch ‡ attempted to explain the effect in another way. His explanation depends on the fact that the electrons possess a magnetic moment which tends to set itself in the direction of the magnetic field. The direction of spin of the electron, however, is connected with its state of motion by the Pauli principle. Two electrons with their spins in the same direction cannot be in the same state of motion. Thus the application of a magnetic field causes a change in the velocity distribution of the electrons, which must also manifest itself in the conductivity. If this explanation were the right one, the longitudinal effect would immediately be intelligible, for this effect of the magnetic field is by its nature entirely independent of the direction of the field in space.

On working the problem out, however, it was found that this method not only gives a result whose order of magnitude is much too small, but is just as incapable of explaining the deviation from the quadratic law. For the quadratic law will always hold in cases where we may confine ourselves to the first term in the expansion in powers of the intensity of the field, i.e. when the higher terms are small compared with the first. This will always be the case if the number of electrons orientated by the magnetic field is small compared with the total number of free electrons. A direct estimate of the former number can readily be obtained from paramagnetic theory, and we find that the condition mentioned holds for much higher fields than those for which the quadratic law ceases to be empirically valid.

This method, then, is not practicable either, and the only remaining way of explaining the phenomena is by the curvature of the paths of the electrons (mentioned at the beginning of this

* P. Kapitza, *Proc. Roy. Soc., A*, **123**, 292 (1929).

† W. Meissner and H. Scheffers, *Phys. Zeitschr.*, **30**, 827 (1929).

‡ F. Bloch, *Zeitschr. f. Physik*, **53**, 216 (1929).

paper (p. 71)) which arises from the Lorentz or ponderomotive force. In what follows we shall discuss how far such an explanation is possible.

The most interesting question to begin with is how far we can explain the way in which the change of resistance depends on the intensity of the magnetic field, and in particular the magnitude of the fields for which deviations from the quadratic law begin to occur (which we shall in future call the "critical intensity"). For this purpose we must consider how far we may regard the magnetic field as causing a slight perturbation of the motion of the electrons. If we regard the electrons as entirely free, they describe arcs of circles in the magnetic field. Thus when the paths are closed, i.e. when the radius of curvature is smaller than the dimensions of the piece of metal, they are quite distinct from the rectilinear paths when there is no field. On superficial consideration, therefore, one would expect that the critical intensity would be given by the condition that the radius of the path is of the order of these dimensions. The values obtained in this way are much too small and, moreover, depend on the size of the piece of metal.

Instead of this we must regard the electrons as not entirely free but as colliding from time to time with the atoms of the lattice. Thus the electrons describe zig-zag paths, and the paths described in the magnetic field will exhibit only slight deviations from these if the motion is approximately rectilinear between two collisions, i.e. if the radius of curvature is large compared with the mean free path of the electrons. As we know, the angular velocity of the electrons is

$$\nu_0 = \frac{eH}{2\pi mc}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where H is the intensity of the magnetic field, e and m the charge and mass of the electron, and c the velocity of light. Thus the radius of the path and the velocity are connected by the relationship

$$r = \frac{mc\nu}{eH};$$

on the other hand, the mean free path is obtained from the conductivity by the equation

$$l = \frac{h\sigma}{2e^2n},$$

where l is the mean free path, σ the conductivity, n the number of

electrons per unit volume, and v their velocity, for which we have to insert the velocity of those electrons which are concerned in conduction. According to Sommerfeld, they are those with the velocity

$$v = \frac{h}{m} \left(\frac{3n}{8\pi} \right)^{\frac{1}{3}},$$

so that we obtain intensities of the order

$$H \sim \frac{enc}{\sigma}.$$

The values of this quantity for gold at various temperatures are tabulated below, along with the empirical values of the critical intensity obtained from the experiments of Meissner and Scheffers. (For this comparison we must not choose the constant b given by Meissner and Scheffers, which is determined by prolonging the linear part of the curve till it intersects the x -axis, and which is less than the critical intensity.)

T	H (theor.)	H (exp.)
78.5°	$3 \cdot 10^5$	$> 10^4$
20.4°	9000	5000
4.2°	400	600

Quantitative agreement, of course, is not to be expected, as this critical intensity is not susceptible of exact definition at all. The comparison shows that the intensities for which the quadratic law is transformed into the linear law are of the order of magnitude anticipated, and also that the behaviour at different temperatures becomes intelligible.

A similar agreement is also obtained for most of the substances which have been investigated by Kapitza. Deviations are exhibited only by substances of the bismuth type, and by semi-conductors like Ge. In neither case are the anomalies very astonishing, as bismuth behaves quite differently from the other metals as regards all magnetic phenomena (e.g. diamagnetism, the Hall effect), so that we are driven to conclude that in its case some other phenomena which hitherto have not been taken into consideration must play a part. In the case of semi-conductors, the idea of free electrons,

on which our evaluation depends, cannot be regarded as an approximation at all.

This evaluation says nothing about the detailed mechanism of the change of resistance; the fact remains that the effects of the magnetic field taken into account by Sommerfeld give far too small a result. We must therefore consider the points which are neglected in Sommerfeld's discussion of the conductivity.

In order to go about this in the right way we must first understand how it is that the very clear way of picturing the phenomena which we have described above should result in so small a change in the resistance. Sommerfeld considers the velocity distribution of the electrons, which in a metal acted on by no external field is, as we know, such that there are

$$f_0 \left\{ \frac{m}{2} (\xi^2 + \eta^2 + \zeta^2) - E_0 \right\} = \frac{1}{e^{\left\{ \frac{m}{2} (\xi^2 + \eta^2 + \zeta^2) - E_0 \right\} / kT} + 1}$$

electrons with velocity components ξ , η , ζ . f_0 is the well-known Fermi function, which, in the case of degeneration ($kT \ll E_0$), is equal to unity, provided $\frac{1}{2}mv^2 < E_0$, and equal to zero for $\frac{1}{2}mv^2 > E_0$. If an electric field F is applied in the direction of the x -axis this distribution is modified, and takes the form

$$f = f_0 + \xi \cdot \chi(E). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

χ is determined from the stationary condition. The increase in the number of electrons with velocity ξ , η , ζ ,

$$\frac{e}{m} \cdot F \cdot \frac{\partial f}{\partial \xi},$$

must in fact be exactly balanced by the scattering at the atoms of the lattice. As regards this scattering it is assumed that a definite proportion of the electrons experience a collision during unit time, and that, though the magnitude of the velocity is the same after the collision as before, all directions are equally probable for the subsequent motion, no matter what the direction of motion before the collision was. (This last assumption makes little difference to the results.) We thus obtain

$$eF \cdot \frac{\partial f}{\partial \xi} = w \int [f(\xi', \eta', \zeta') - f(\xi, \eta, \zeta)] d\Omega',$$

where the integration is to be taken over the surface of the sphere

with radius $\sqrt{\xi^2 + \eta^2 + \zeta^2}$, as the stationary condition. Together with (2), this gives

$$eF \cdot \xi \cdot \frac{\partial f_0}{\partial E} = -4\pi w \cdot \xi \cdot \chi(E), \quad . \quad . \quad . \quad (3)$$

terms of the second order in F being neglected. If a magnetic field H is now applied in the direction of the z -axis, the direction of the electrons will be permanently altered as a result of the Lorentz force; this gives rise to a term

$$\frac{eH}{mc} \left(\xi \frac{\partial f}{\partial \eta} - \eta \frac{\partial f}{\partial \xi} \right)$$

in the stationary condition. If in addition the current is made to flow in the direction of the x -axis, there will be an electromotive force in the direction of the y -axis (the Hall effect), so that we finally have to solve the equation

$$(eF_x \xi + eF_y \eta) \frac{\partial f_0}{\partial E} = w \int [f(\xi', \eta', \zeta') - f(\xi, \eta, \zeta)] d\Omega' - \frac{eH}{mc} \left(\xi \frac{\partial f}{\partial \eta} - \eta \frac{\partial f}{\partial \xi} \right). \quad . \quad (4)$$

If, in particular, w is independent of the velocity, the equation is still satisfied by an expression of type (2). For if we substitute (2) in (4), the terms multiplied by ξ again give the conditions (3), while the terms in η give the equation

$$eF_y \cdot \frac{\partial f_0}{\partial E} = \frac{eH}{mc} \cdot \chi(E).$$

If $F_y = -\frac{eH}{4\pi w mc} F_x$, the two equations are identical, i.e. (4) has a solution of type (2). It is at once clear that in this case the resistance is strictly independent of H . In actuality w will depend on the velocity, but $\partial f_0 / \partial E$ differs markedly from zero only in the neighbourhood of $E = E_0$, so that practically only one velocity plays an important part. If we bear in mind that the degeneration is not complete, i.e. that $\partial f_0 / \partial E$ still differs from zero in a region of order (kT) , we do obtain an effect, which is, however, of the relative order of magnitude $(kT/E_0)^2$ and was calculated by Sommerfeld.

A deviation from this behaviour may be due to various circumstances. In the first place, a more accurate calculation might show that the probability of a collision occurring is itself modified by the

magnetic field. More detailed consideration shows that here we are concerned not with the probability of collision but with the change of momentum which an electron is most likely to experience within a given time. In the second place, some part may be played by the fact that according to quantum mechanics the various components of the velocity are no longer interchangeable when a magnetic field is present, so that it is no longer permissible to speak of a velocity distribution at all. Finally, the fact that the electrons are really not free at all but are moving in a periodic potential field has not been taken into consideration hitherto. The effect of this potential field may not be reckoned as included in that of the collisions, for we know that the conductivity is infinite if the field is strictly periodic. The effect of this periodic field is rather that the simple relationship between the energy and the velocity is destroyed, so that the stationary condition is considerably modified.

We shall begin by considering the first possibility.* So long as we regard the processes giving rise to a finite resistance as collisions with point-centres, it is at once clear that the magnetic field cannot lead to a modification of the probability of collision, for it is only the instantaneous motion of the electron that is concerned in the collision.

We know,† however, that these processes are due, at low temperatures at least, to the thermal vibrations of the atoms of the lattice, which according to Debye may be regarded as the vibrations of a continuous elastic body. So long as the temperature is high compared with the characteristic temperature of the substance in question, these vibrations may be calculated by the classical statistics, but it must be borne in mind that the spectrum of these vibrations must break off at a definite minimum wave-length of the order of magnitude of the interatomic distances. Interaction with these lattice vibrations, as an easy calculation shows, has an effect not like that of collisions with point-centres of scattering, but like that of collisions with centres of scattering which on the average have dimensions of the order of the distances between the atoms.

The change in the scattering mechanism when an external mag-

* The following account differs somewhat from what I said in my lecture, where I made no attempt to decide which of these possibilities corresponds to reality. In the interval between delivering the lecture and writing this report I have been able to show that the two first possibilities are out of the question. I wish to take this opportunity of thanking Drs. Bethe and Frank for some remarks made by them during the discussion and subsequent written communications, which proved very helpful in clearing up these points.

† F. Bloch, *Zeitschr. f. Physik*, **52**, 555 (1928).

netic field is applied will then, as is likewise easily seen, be appreciable only when the curvature of the paths is appreciable within a region of the order of magnitude of the centres of scattering. But in the strongest fields attainable the radii of the paths are of the order of 10^{-5} cm., so that the change in the resistance caused in this way is far too small. Even at very low temperatures the relationships are much the same, although there the lattice vibrations of very small wave-length become "frozen", which means that the centres of scattering become larger. Their magnitude, however, increases in proportion to Θ/T . These considerations, therefore, do not lead to any feasible explanation of the effect.

In discussing the second possibility, it is convenient to start from the limiting case of very strong fields and first of all to write down the exact proper functions for an electron subjected to a magnetic field and then to assume a distribution of electrons not as regards their different velocities but as regards their different stationary states in the magnetic field. The accurate calculation shows that in this case the relationship between the conductivity and the scattering mechanism remains exactly the same, i.e. that we are again concerned with the mean change of momentum of an electron in unit time, and that the conductivity depends on this quantity in the same way as it does in the absence of a magnetic field. In this result, however, we neglect those effects which arise in the statistics as a result of the fact that the spectrum of proper values of electrons in a magnetic field is discrete, since the paths are closed. These effects are the direct expression of the quantum mechanics theorem of the non-interchangeability of the components of velocity. They give rise to corrections depending on $h\nu_0/kT$. ($\nu_0 = eH/2\pi mc$ is twice the Larmor frequency, i.e. the angular velocity of the electrons in the magnetic field). In all cases occurring in practice this quantity is certainly small; it is therefore permissible to expand in powers of this quantity; for reasons of symmetry, the odd powers must again vanish. Thus here we may only expect a correction of the order $(h\nu_0/kT)^2$, which is much smaller than the change of resistance observed. On the other hand, we may expect a new anomaly in the relationship between the resistance and the magnetic field to arise whenever we use fields which are of the order of magnitude $2\pi kTmc/e$. It does not seem impossible that fields of this order should be reached at low temperatures.

At any rate we see that the two first possibilities are incapable of explaining the effect. The third possibility has hitherto not been

discussed in detail, but we can see that such an effect must exist, and that it is of the right order of magnitude.

In fact, the deviation in the motion of the electrons from that of free electrons, which is caused by the periodic potential field of the atoms of the lattice, manifests itself in a change in the relationship between the energy and the velocity. In some metals this change even has a decisive effect on the sign of the Hall effect.* If we take this into account in the stationary condition (4), we see that (2) will no longer satisfy the equation. We must, on the contrary, regard (2) as the beginning of a power series in which higher terms must be included. We then obtain additional terms, such as products of the form $\xi\eta^2$, &c., and the equation may no longer be solved in the simple way possible with (4). Thus we see that the change in resistance no longer vanishes, even when the probability of collision is strictly the same for all electrons.

We may obtain the order of magnitude as follows: in Sommerfeld's theory it was the "first order" effect that vanished, and we had to include higher terms in kT/E_0 . Here even the first order effect will differ from zero. Thus here this effect is caused solely by the deviation from the motion of free electrons, i.e. it is proportional to a quantity κ giving the relative deviation. In all, then, it will differ from Sommerfeld's result by a factor $\kappa(E_0/kT)^2$. To obtain the order of magnitude observed, we must assume that κ lies between 0.1 and 0.01, an assumption which seems entirely reasonable.

This explanation is also in agreement with experiments by Schubnikow and de Haas,† according to which the change of resistance in a single crystal resulting from a change in the inclination to the crystal axes is of the same order of magnitude as the total change of resistance. This seems intelligible if the whole effect arises solely from the anisotropy of the motion of the electrons.

If the magnetic field is parallel to the current we should expect an effect of the same order of magnitude as in the transverse case, as the sole reason for supposing otherwise is based on the ideas that the three components of the motion of the electron are separable and that the component parallel to the magnetic field is not affected by this field, neither of which statements is true for the periodic field of force.

More detailed investigation shows that according to this model

* R. Peierls, *Zeitschr. f. Physik*, **53**, 255 (1929).

† L. Schubnikow and W. J. de Haas, *Proc. Amst. Acad.*, **33**, 360 (1930).

the resistance increases asymptotically towards a constant value for fields of high intensity.*

As a result of these considerations, then, we may say that the fact that the quadratic law ceases to be valid at a definite field intensity, and the actual magnitude of this field intensity, are alike intelligible. The essential explanation of the effect lies not in the forces acting on the electronic spin, but in the Lorentz force which affects the motion of the electron in its path. An effect of the correct magnitude, however, is not obtained unless the forces to which the electron is subjected in the metal are also taken into account.

* N. H. Frank (*Zeitschr. f. Physik*, **64**, 650 (1930)), shows that this result is consistent with the empirical data.

AUTHOR INDEX

- Berger-Davis, 31.
 Bethe, H., 13, 17, 25, 35, 36, 37, 38, 39, 41, 44, 77.
 Bewilogua, L., 14.
 Bloch, F., 45, 46, 47, 48, 49, 54, 55, 60, 72, 77.
 Boas, W., 5, 7, 10.
 Borelius, G., 46, 51.
 Bragg, W. H., 30.
 Bragg, W. L., 18, 30.
 Brillouin, L., 47, 48, 49.
 Brindley, 21.
 de Broglie, L., 1, 34, 35, 36, 39.

 Clay, 52.
 Clusius, K., 53.

 Darwin, C. G., 25, 27, 29, 32, 36.
 Davisson, C. J., 1, 3, 4, 5, 32, 35.
 Debye, P., 14, 22, 24, 32, 46, 47, 49, 50, 51, 53, 59, 77.
 Drude, 63.
 Dymond, 43.

 Ehrenberg, 30, 31.
 Einstein, A., 47, 55.
 Eucken, A., 57, 62.
 Ewald, 25, 27, 28, 29, 30, 32, 36.

 Farnsworth, 6.
 Frank, N. H., 77, 80.
 Frenkel, J., 45, 53.

 Gajewski, H., 14.
 Gerlach, W., 54.
 Germer, L. H., 1, 3, 5, 32, 35.
 Goens, E., 55, 58, 59, 61.

 Goldschmidt, V. M., 20, 21.
 Gordon, 42.
 Grüneisen, E., 46, 55, 57, 58, 61.

 de Haas, W. J., 79.
 Harteck, P., 53.
 Hartree, 42.
 Heisenberg, W., 66, 68.
 Heitler, 65, 66.
 Hopf, L., 47.
 Houston, W. V., 45, 54, 55.

 James, 32.

 Kapitza, P., 56, 72, 74.
 Kikuchi, 13, 34.
 Kluge, W., 7.

 von Laue, M., 2, 8, 25, 26, 27, 34, 37, 38.
 London, 65, 66.
 Lonsdale, 21.
 Lorentz, 63.

 Madelung, E., 50, 55.
 Mark, H., 13, 17, 43.
 Matthiessen, 51.
 Mayer, G., 30.
 Meissner, W., 46, 52, 56, 58, 72, 74.
 Mirolubow, N., 45, 53.
 Mott, N. F., 13, 26.

 Onnes, K., 52.

 Patterson, 35.
 Pauli, 68.
 Peierls, R., 45, 54, 55, 57, 58, 59, 60, 62, 64, 79.

- Polanyi, M., 26.
Ponte, M., 1, 13, 34.
Prins, 33.

Rose, D. C., 7.
Rupp, E., 2, 3, 4, 5, 6, 7, 8, 11, 13, 25, 34.
Rutherford, E., 18.

Scheffers, H., 56, 72, 74.
Schrödinger, E., 35, 36.
Schubnikow, L., 79.
Siegbahn, 27, 29, 31, 34, 35.
Sommerfeld, A., 7, 45, 63, 68, 69, 71, 72, 74, 75, 76, 79.

Stenström, 27, 29, 31, 35.
Susich, 31.
Szczeniowski, S., 7.

Thomson, G. P., 13, 34.
Thomson, J. J., 42.
Tuyn, 52.

Vogt, E., 51.

Waller, J., 29, 32.
West, J., 18.
Wierl, R., 13, 17, 25, 34, 38, 43.
Wolf, K., 38, 39.

SUBJECT INDEX

- Anomalous dispersion of electrons, 3, 4, 5.
 — — of X-rays, 32.
- Atom form factor, 15, 16-19, 22, 26, 28, 38, 39, 41-44.
- Benzene, interatomic distances in, 21.
- Benzenes, di-substituted, 23.
- Bethe's dispersion theory of electron diffraction, 17, 25, 36-39.
- Bose-Einstein statistics, 67.
- Bragg reflection, 16, 26, 28, 29, 34, 35.
- Bragg's angle, 26, 28, 29.
- de Broglie's equation, 1, 2, 13, 34.
- de Broglie's theory of electron interference, 34.
- de Broglie waves, 36, 39.
- Bromo-ethane, 23.
- Cis-trans* isomerism, 22, 23.
- Compton effect, 32, 43.
- Conductivity, electrical, *see* Electrical resistance.
- , thermal, *see* Thermal resistance.
- Critical intensity of strong magnetic fields, 73.
- Crystals, diffraction of electrons by, 31, 34-39.
- , electrical conductivity of, 8-11.
- , temperature effect, 9.
- Crystals, internal potential of, 3-11, 13, 27, 35, 38, 39.
- , mosaic structure in, 29, 30.
- , reflection of electrons from, 2-3, 6, 31, 38, 39.
- Cyclohexane, structure of, 22.
- Cyclopentane, interatomic distances in, 21.
- Darwin-Ewald dispersion theory of X-rays, 25, 27-34.
- Debye's function, 46, 49, 51, 59.
- Debye's method for interatomic distances, 14-16, 24.
- Debye-Scherrer rings, 17.
- Dichloro-ethane, 23, plate.
- Dichloro-ethylene, 22, 23.
- Dichloropentane, 22.
- Dispersion theory of electron diffraction, 17, 25, 36-39.
- Dispersion theory of X-rays, 25, 27-34.
- —, tests of, 30.
- Electrical resistance and collisions, 64.
- — and temperature, 45-57, 61-62.
- —, anisotropy of, 55.
- —, Bloch's theory of, 46, 49, 54, 55, 60.
- —, Peierls' extension to Bloch's theory of, 54, 55, 57.
- —, Brillouin's theory of, 47, 48.
- —, Houston's theory of, 54, 55.
- —, ideal, 51, 54, 62.
- — in strong magnetic fields, 71-80.
- — of crystals, 8-11.
- — of crystals and apparent internal potential, 11.
- — of crystals and temperature, 9.
- — of metals, numerical data, 52, 53.
- —, residual, 51, 52, 54, 58, 62.
- Electron diffraction, 1, 13, 34.
- — and chemical decomposition, 23.
- — and *cis-trans* isomerism, 22, 23.
- — and homogeneous gas reactions, 23.
- —, Bethe's dispersion theory of, 17, 25, 36-39.
- — by carbon tetrachloride vapour, 20, plate.
- — by crystals, 31, 34-39.
- — in beam of vapour, 19-23.

- Electron interference, de Broglie's theory of, 34.
 — — in crystals, 1.
 — — in free molecules, 13-24.
 Electron theory of metallic conduction, Sommerfeld's, 7, 45, 63, 71, 72, 75, 79.
 — —, deviations from, 77-79.
 Electron waves, investigation of molecular structure by, 14.
 Electrons, anomalous dispersion of, 3, 4, 5.
 —, fast, 1, 13, 34, 36.
 —, free mobility of, 63, 64, 69, 73.
 —, mutual action of, 63-69.
 —, reflection of, 2-3, 6, 31, 38, 39.
 —, refractive index for, 1-3, 13, 35, 36, 37.
 —, scattering of, *see* Scattering.
 —, slow, 1, 13, 35, 37.
 —, specific heat of, 45, 68, 69.
 Exclusion principle, 65, 67, 68, 72.
- Fermi statistics, 45, 63, 71.
 Ferro-magnetism, Heisenberg's theory of, 66, 68.
 Forbidden reflections, 30, 39.
 Free mobility, 22, 23.
 — — of electrons, 63, 64, 69, 73.
- Hall effect, 76, 79.
- Intensity of scattering, *see* Scattering.
 Interatomic distances in benzene, 21.
 — — in cyclopentane, 21.
 — — in tetrachlorides, 20, 21.
 Interference of electrons, *see* Electron interference.
 — of X-rays, *see* X-ray interference.
 Internal potential, 3-11, 13, 27, 35, 38, 39.
 — — and potential difference, 4-7, 9.
 — — and reflecting crystal surface, 10.
 — — and temperature, 7, 9.
 — — and the work function, 7, 8.
 Internal potential, apparent, 9.
 — and electrical conductivity, 11.
 Internal potential as criterion of insulator, 10.
 — — in metallic crystals, 4-8.
 — — in non-metallic crystals, 8-11.
- Laue's kinematic theory of X-ray interference, 25-27, 29, 30, 33, 34, 35.
- Magnetic fields and electrical resistance, 71-80.
- Metallic conduction, Sommerfeld's theory of, 7, 45, 63, 71, 72, 75, 79.
 — —, deviations from, 77-79.
 Molecular structure, investigation by electron waves and X-rays, 14-24.
 Molecular structure of cyclic compounds, 15, 16.
 — — of tetrachlorides, 15, 16.
- Oxalyl chloride, 23.
- Paramagnetism, feeble, 68.
 Polanyi's layer line relationship, 26.
 Potential, internal, *see* Internal potential.
 Potential difference, effect on internal potential, 4-7, 9.
- Raman effect, 32, 43.
 Reflection of electrons, 2-3, 6, 31, 38, 39.
 — of X-rays, 31.
 Refractive index for electrons, 1-3, 13, 35, 36, 37.
 — — for X-rays, 27, 31, 33, 35.
- Resistance, *see* Electrical resistance, Thermal resistance.
- Rutherford's scattering formula, 16, 19, 42.
- Scattering, comparison of electrons and X-rays, 18, 19.
 —, elastic, 13, 17.
 —, inelastic, 13, 39, 43.
 — — and dispersion theory, 33.
 —, nuclear, 17, 18, 19.
 — of electrons and atomic number, 17.
 — — by cyclopentane, 16, 17, 18.
 — — by metal foils, 17, 18, plate.
 — —, intensity of, 13, 15, 16, 18, 26, 41-44.
 — —, Rutherford's formula for, 16, 19, 42.
 — of X-rays by vapour, 14, 15.
 — —, intensity of, 15, 16.
- Schrödinger's equation, 35, 36.
 Screening constant, 17.
 Screening effect, 63, 64.
 Secondary spectra, 30.
 Sommerfeld's theory of metallic conduction, 7, 45, 63, 71, 72, 75, 79.
 — —, deviations from, 77-79.
- Spin, 65, 66, 67, 69, 72.
 Structure factor, 29.
 Superconduction, 45, 56.
- Temperature and electrical resistance, 9, 45-57, 61-62.
 — and internal potential, 7, 9.
 — and thermal resistance, 57-62.
 — and total reflection, 32.

- Tetrachlorides, interatomic distances in, 21.
- Thermal resistance and lattice deformation, 61, 62.
- — and temperature, 57-62.
- — of insulating crystals, 57.
- — of metals, 58, 59, 60.
- — , Peierls' theory of, 57, 62.
- Total reflection, breadth of region of, 28, 29, 31.
- , effect of temperature on, 32.
- Wiedemann-Franz-Lorenz law, 61.
- Wiedemann-Franz-Lorenz quantity, 57, 58, 60.
- Work function and internal potential, 7, 8.
- X-ray interference, Laue's kinematic theory of, 25-27, 29, 30, 33, 34, 35.
- X-rays, anomalous dispersion of, 32.
- , dispersion theory of, 25, 27-34.
- , reflection of, 31.
- , refractive index for, 27, 31, 33, 35.
- , scattering of, *see* Scattering.

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